Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Is basicity the sole criterion for attaining high carbon dioxide capture in deep-eutectic solvents?

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1. Synthesis of DESs

Choline chloride- ([ChCl]-) and tetrbutylammoinium bromide- ([TBAB]-) based DESs were prepared by complexing them with desired HBDs, at a certain molar ratio at 80 ^{o}C for 4h. Diethylenetriamine- ([DETA])-based DESs were prepared in two steps. The first step involved protonation of DETA by the dropwise addition of hydrochloric acid under vigorous stirring at 0^{o}C in 1:3 mole ratio. The resultant protic ionic liquid (PIL) was subject to rotary evaporator under reduced pressure and subsequently to ultra-vacuum at 60 ^{o}C for 6h to remove water vapour and other volatile impurities. The second step involved the complexation of the PIL with suitable HBDs to get the DESs. The synthesized DESs were characterized by the ^{1}H- and ^{13}C-NMR spectroscopic methods (see entry 2). The water content of the resulting DES, as measured by the Karl-Fisher Coulometer, were below 40 ppm before experiment. The thermal stability of the synthesised DESs as obtained by the thermogravimetric analysis (TGA) were between 110 – 240 ^{o}C (see Fig S1 – S9). All DESs exhibited lower melting point as shown by their differential scanning calorimetry (DSC) profiles (see Fig S10 – S18). The anomalies in the ^{1}H- and ^{13}C-NMR spectra post CO_2 absorption is shown in the entry 6 and Fig S28 – S31.

2. Characterization of DESs

[ChCl][EA] = 1:6

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 2.64 (*t*, CH_2-OH), 3.1 (*s*, N-CH_3), 3.43 (*t*, HO-CH_2), 3.51 (*t*, CH_2-NH_2), 4.0 (*m*, N-CH_2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 42.2, 53.8, 55.5, 63.0 and 67.4.

[ChCl][DEA] = 1:12

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 2.61 (*t*, CH_2-OH), 3.0 (*s*, N-CH_3), 3.4 (*t*, HO-CH_2), 3.56 (*t*, CH_2-NH_2), 3.9 (*m*, N-CH_2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 49.8, 53.9, 55.6, 60.2 and 67.4.

[ChCl][TEA] = 1:3

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 2.64 (*t*, CH_2-OH), 3.1 (*s*, N-CH_3), 3.4 (*t*, HO-CH_2), 3.59 (*t*, CH_2-NH_2), 3.96 (*m*, N-CH_2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 30.2, 53.8, 55.6, 58.8 and 67.4.

[TBAB][EA] = 1:5

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 0.87 (*t*, CH_3), 1.29 (*m*, CH_2), 1.57 (*m*, CH_2), 2.64 (*t*, CH_2-OH), 3.12 (*m*, N-CH_2), 3.51 (*t*, CH_2-NH_2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 12.9, 19.2, 23.1, 42.3, 58.1 and 63.0.

[TBAB][DEA] = 1:2

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 0.85 (*t*, CH_3), 1.28 (*m*, CH_2), 1.57 (*m*, CH_2), 2.55 (*t*, CH_2-OH), 3.11 (*m*, N-CH_2), 3.62 (*t*, CH_2-NH_2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 12.8, 19.1, 23.1, 41.7, 58.1 and 58.5.

[TBAB][TEA] = 1:2

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 0.85 (*t*, CH_3), 1.26 (*m*, CH_2), 1.55 (*m*, CH_2), 2.63 (*t*, CH_2-OH), 3.10 (*m*, N-CH_2), 3.58 (*t*, CH_2-NH_2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 12.9, 19.1, 23.1, 55.6, 58.1 and 58.8.

[DETA.Cl][EDA] = 1:4

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 2.66 (*t*, NH_2-CH_2), 2.74 (*t*, $^{+}NH_3$-CH_2-CH_2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 39.4, 41.5 and 49.3.

[DETA.Cl][AP] = 1:4

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 1.65 (*m*, CH_2), 2.58 (*t*, CH_2-NH_2^{+}), 2.65 (*t*, CH_2-NH_3^{+}), 2.74 (*t*, CH_2-OH), 3.54 (*t*, CH_2-NH_2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 31.8, 37.3, 39.4, 49.6 and 59.2.

[DETA.Cl][TEPA] = 1:4

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 2.48 (*q*, CH_2-NH_2^{+}), 2.53 (*q*, CH_2-NH_3^{+}), 2.64 (*m*, NH_2-CH_2-CH_2), 2.72 (*m*, NH-CH_2-CH_2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 36.9, 39.6, 44.8, 49.5, 54.4 and 58.6.

3. Thermogravimetric analysis (TGA) data of DESs

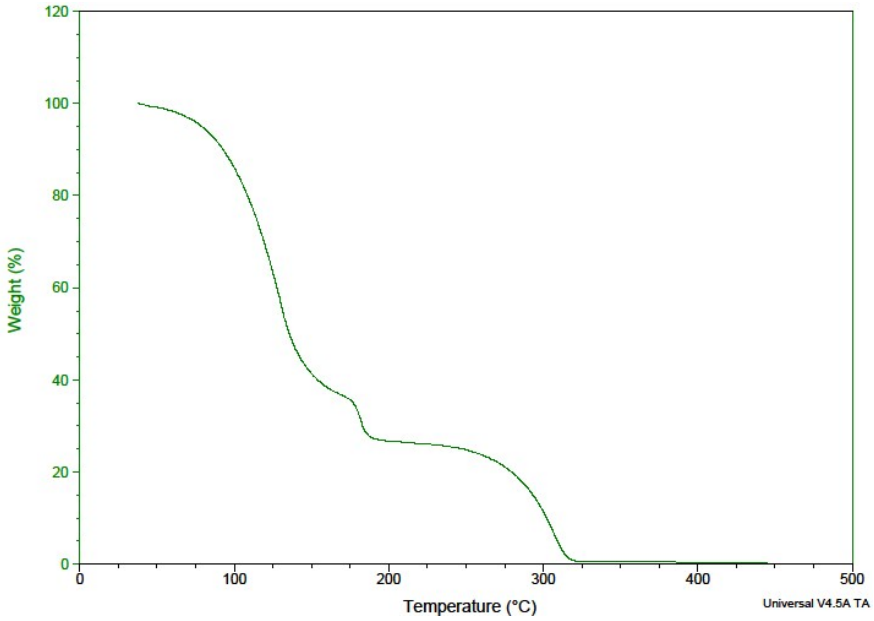


Fig S1. TGA pattern for [ChCl][EA] = 1:6

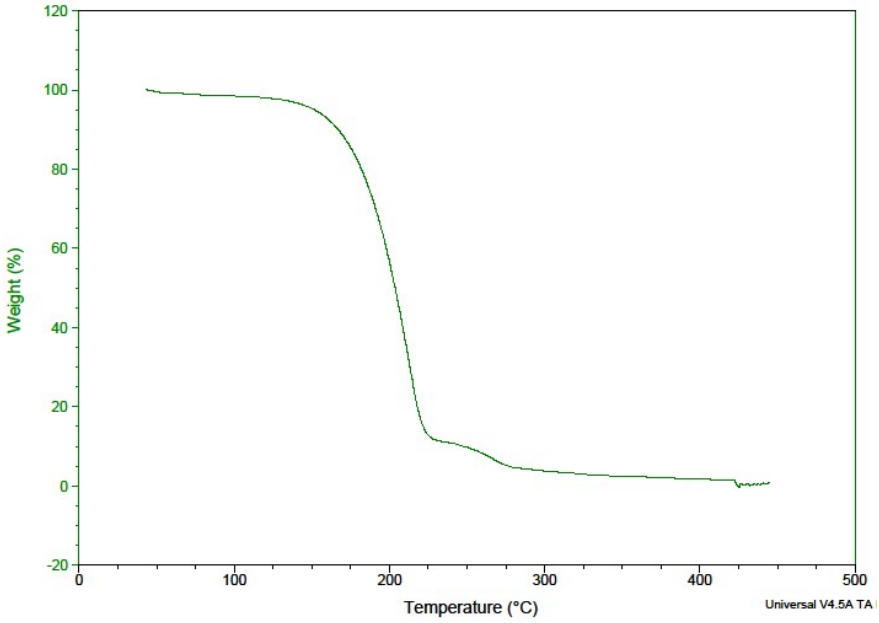


Fig S2. TGA pattern for [ChCl][DEA] = 1:12

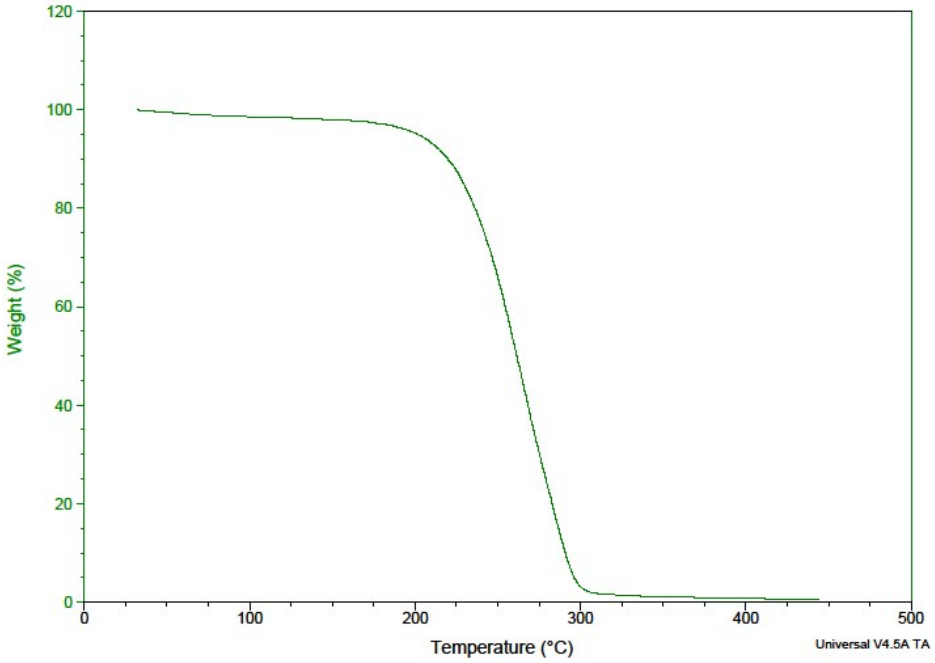


Fig S3. TGA pattern for [ChCl][TEA] = 1:3

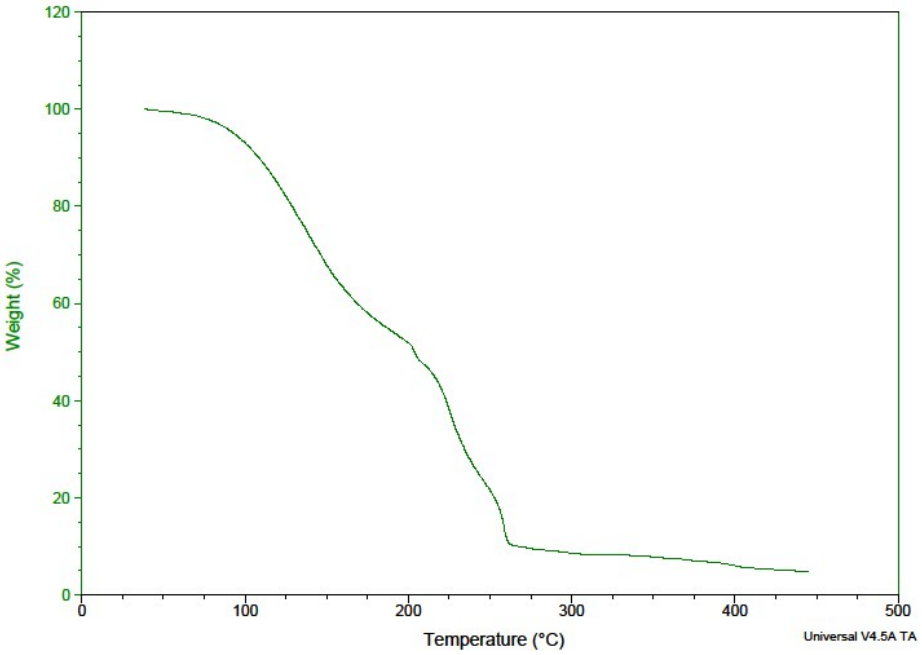


Fig S4. TGA pattern for [TBAB][EA] = 1:5

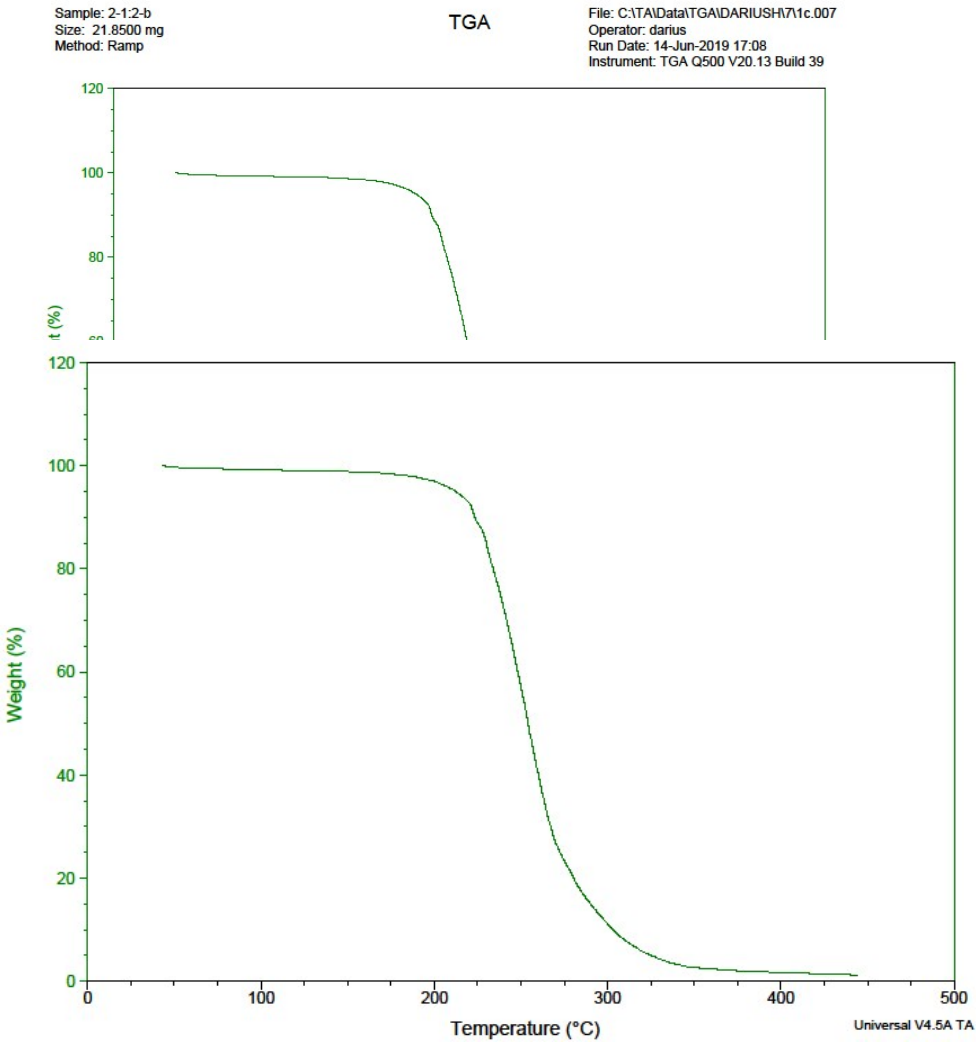


Fig S5. TGA pattern for [TBAB][DEA] = 1:2

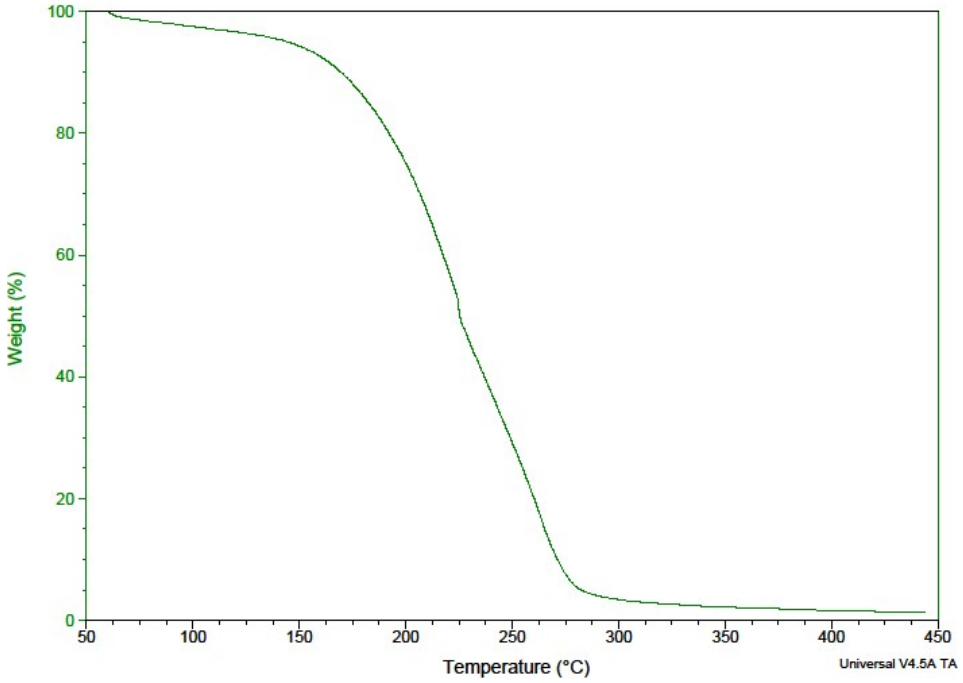


Fig S6. TGA pattern for [TBAB][TEA] = 1:2

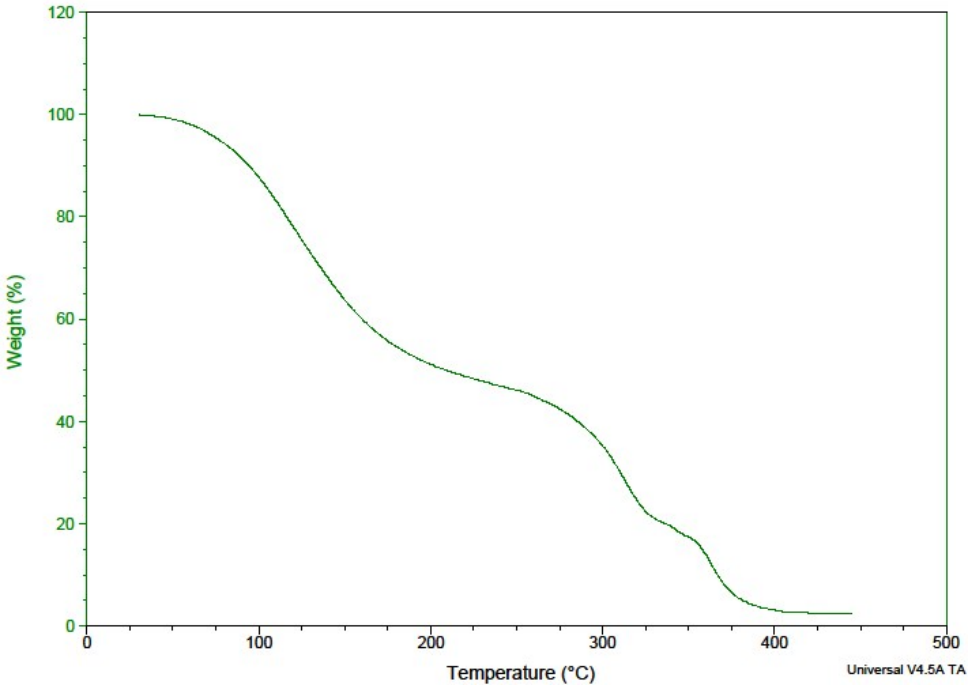


Fig S7. TGA pattern for [DETA.Cl][EDA] = 1:4

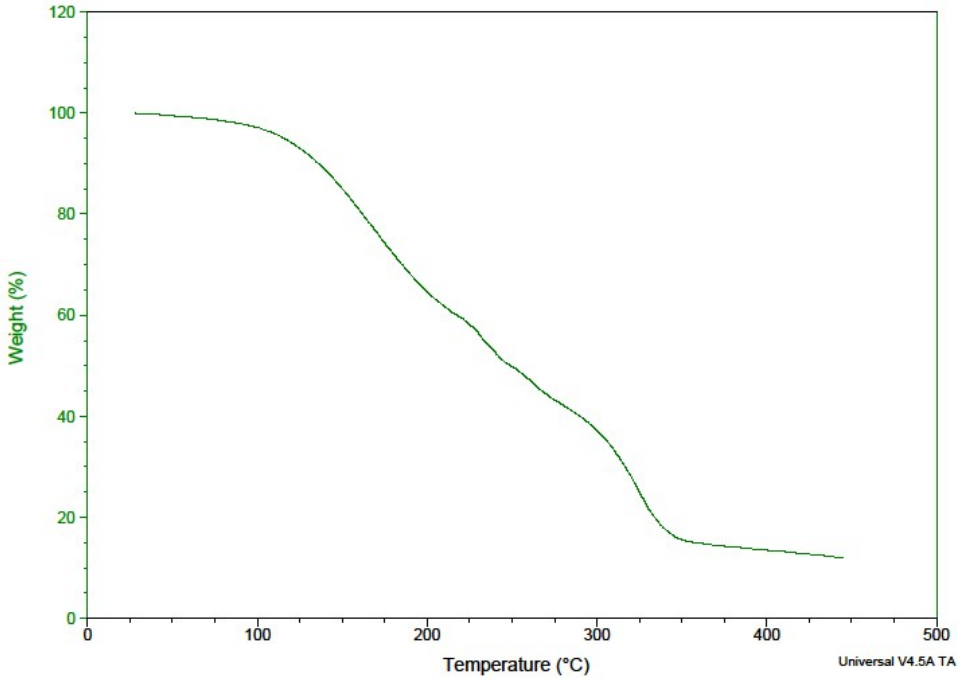


Fig S8. TGA pattern for [DETA.Cl][AP] = 1:4

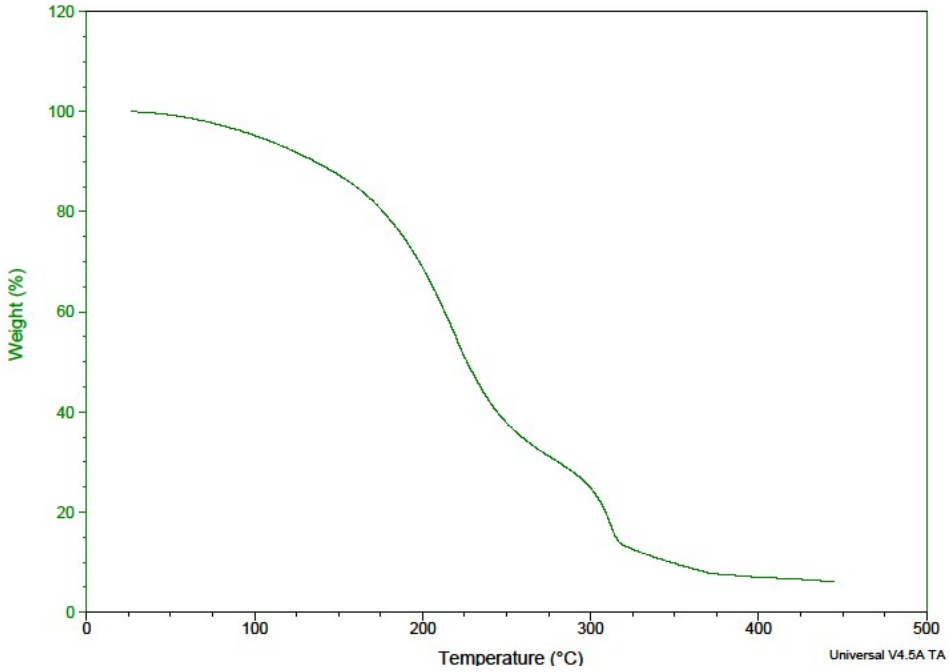


Fig S9. TGA pattern for [DETA.Cl][TEPA] = 1:4

4. Differential Scanning Calorimetry (DSC) data of DESs

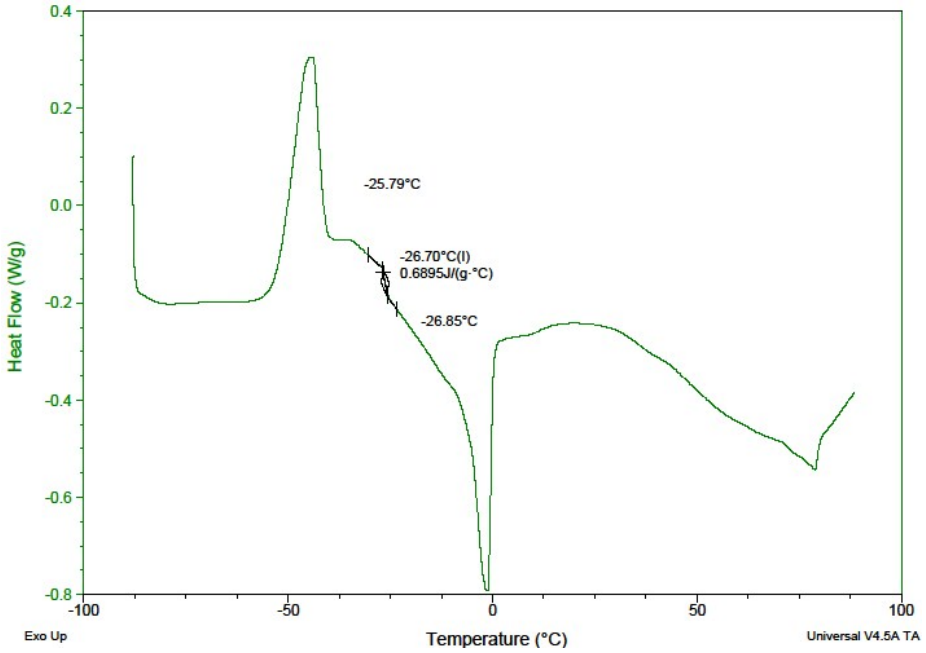


Fig S10. DSC pattern for [ChCl][EA] = 1:6

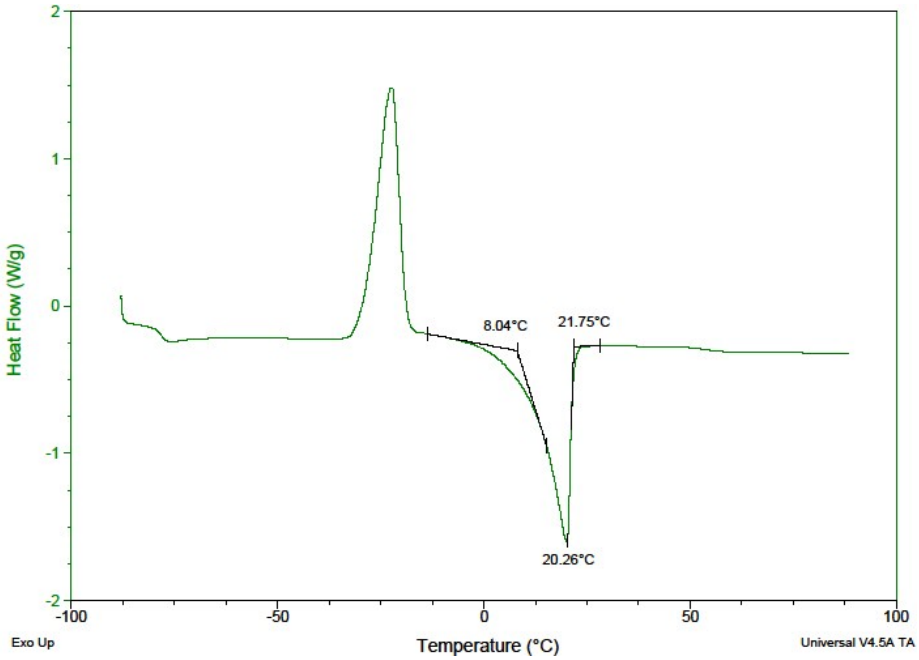


Fig S11. DSC pattern for [ChCl][DEA] = 1:12

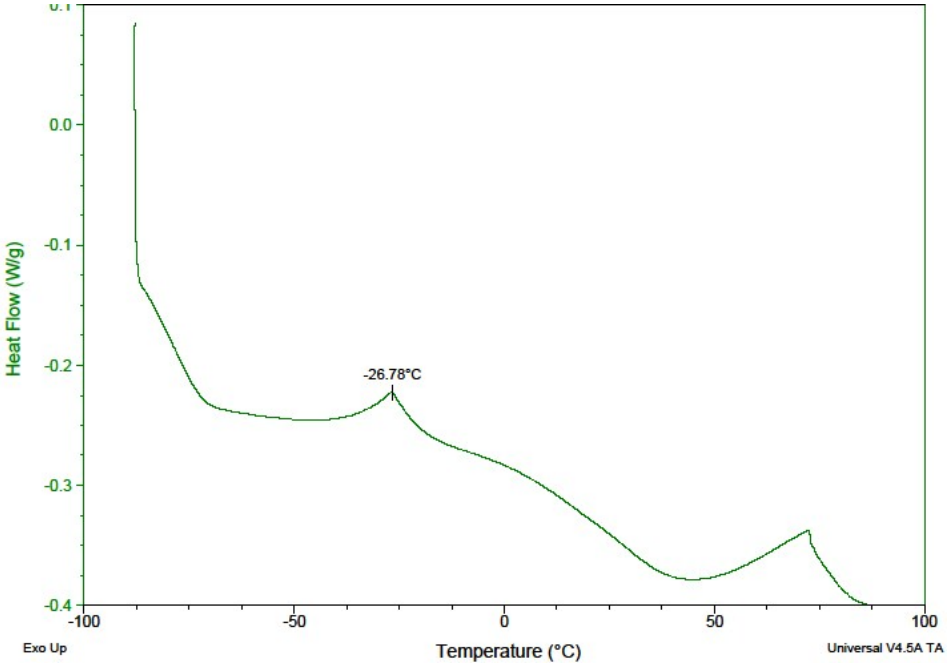


Fig S12. DSC pattern for [ChCl][TEA] = 1:3

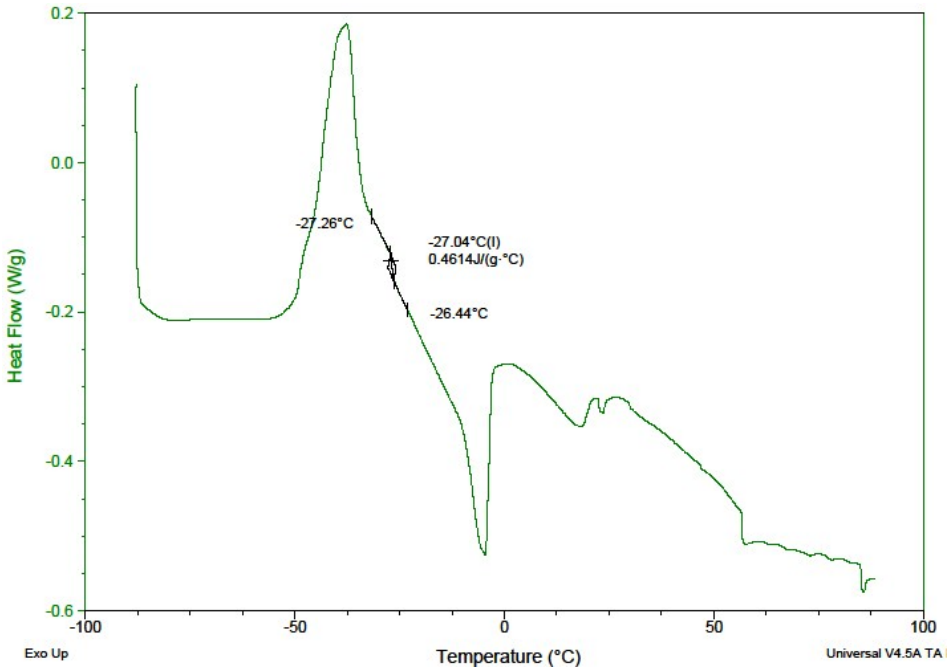


Fig S13. DSC pattern for [TBAB][EA] = 1:5

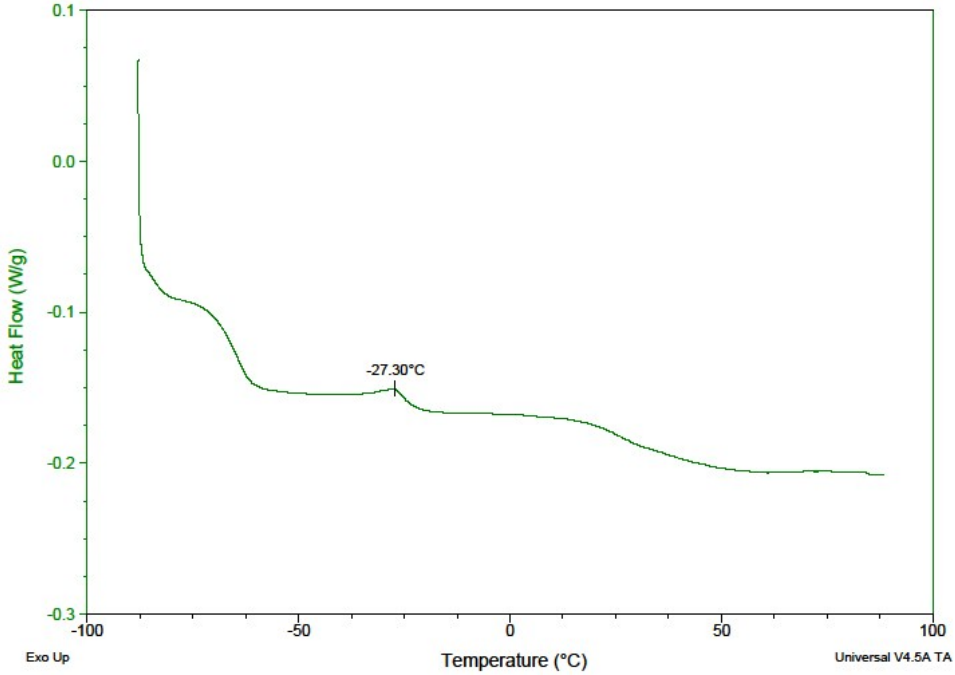


Fig S14. DSC pattern for [TBAB][DEA] = 1:2

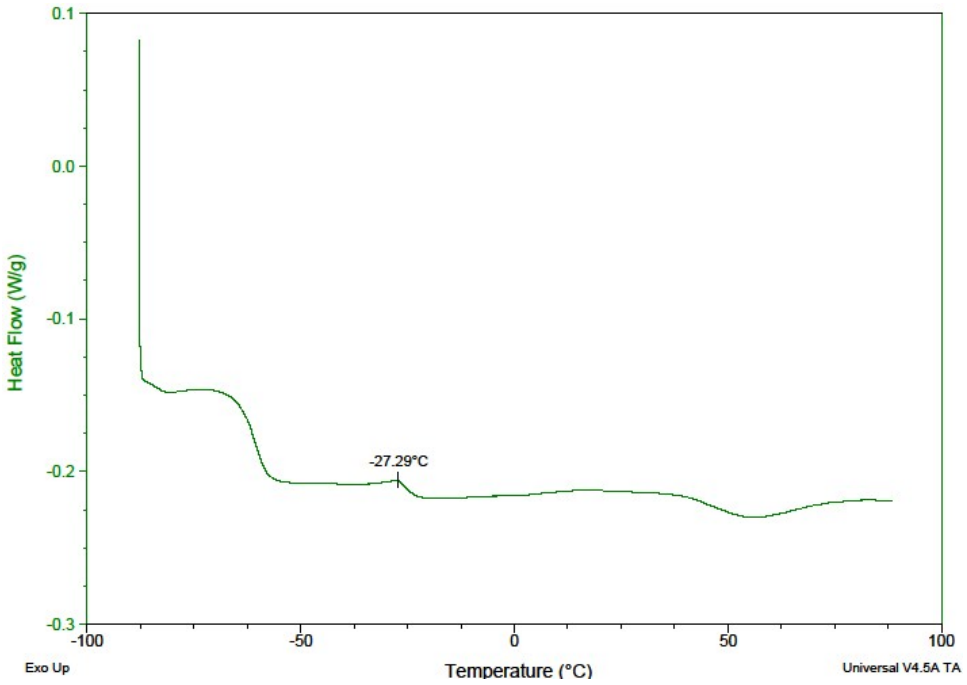


Fig S15. DSC pattern for [TBAB][TEA] = 1:2

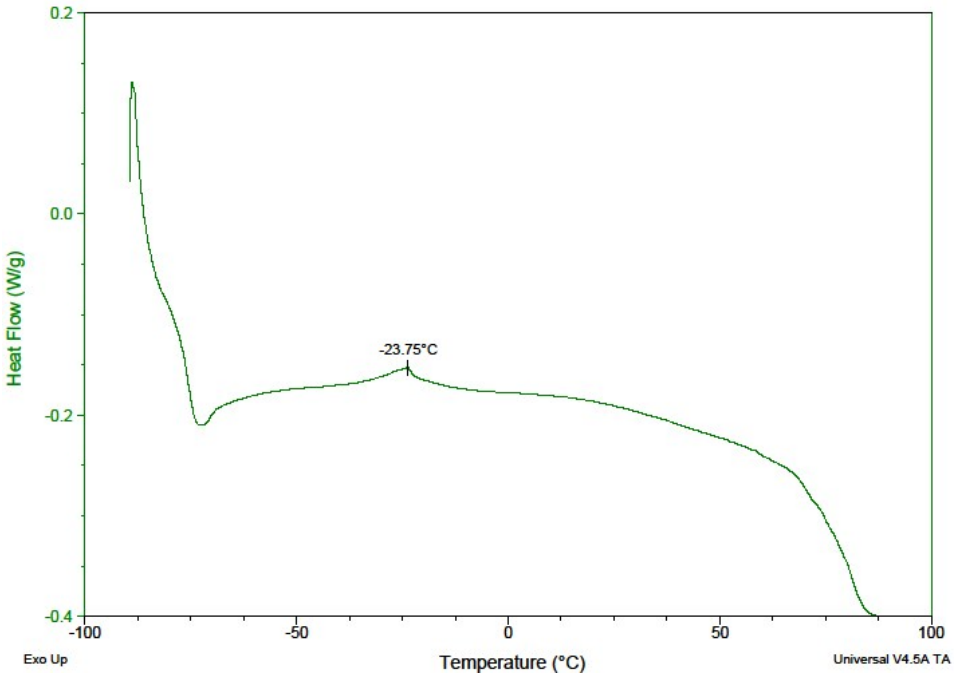


Fig S16. DSC pattern for [DETA.Cl][EDA] = 1:4

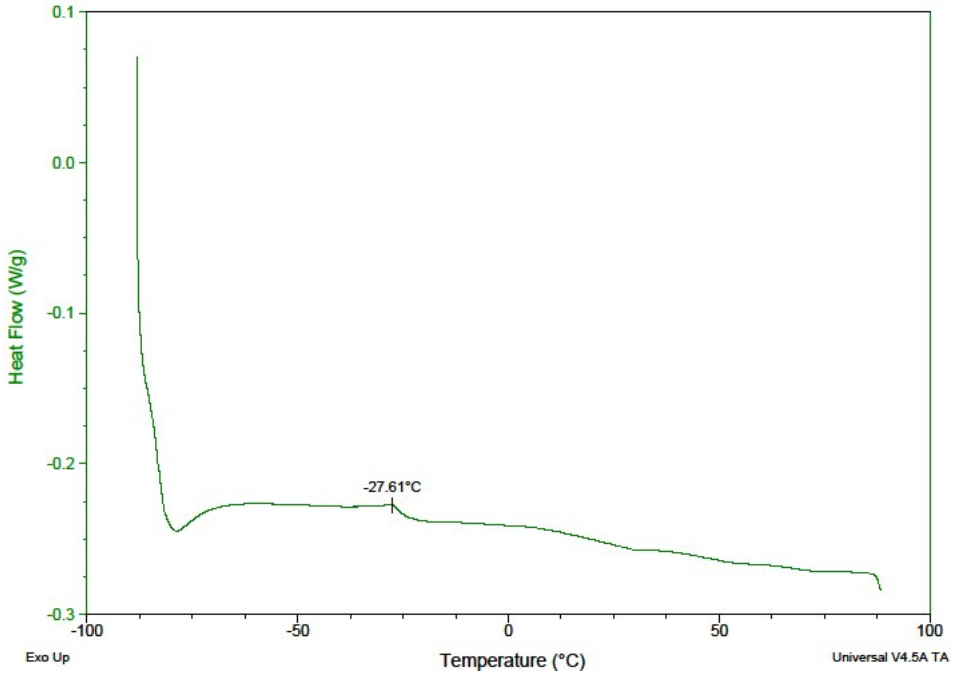


Fig S17. DSC pattern for [DETA.Cl][AP] = 1:4

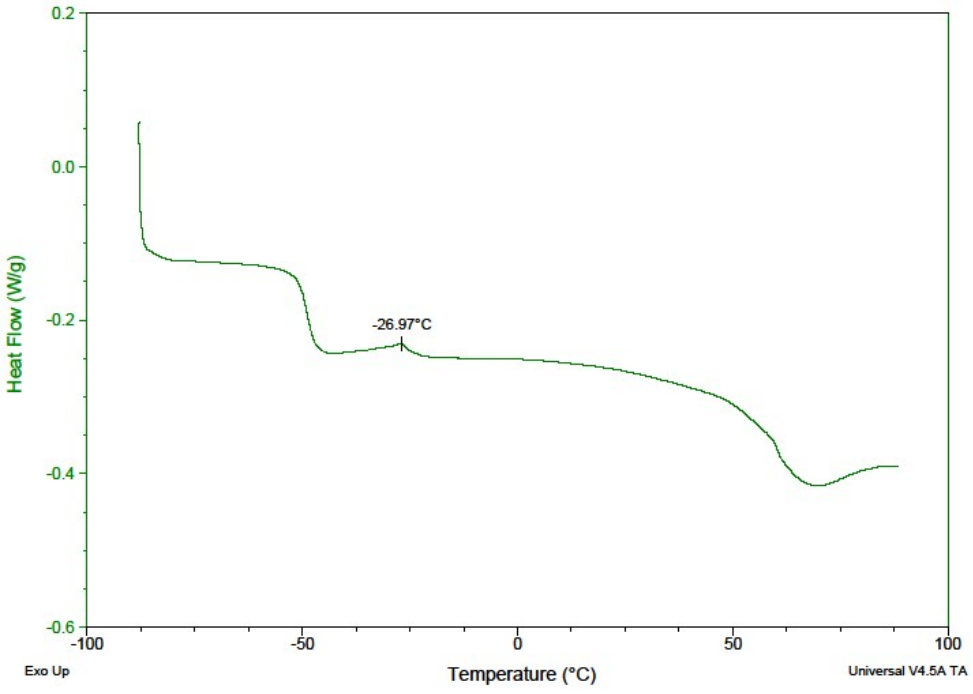


Fig S18. DSC pattern for [DETA.Cl][TEPA] = 1:4

5. ^{13}C-NMR spectrum of DESs before and after CO_2 capture

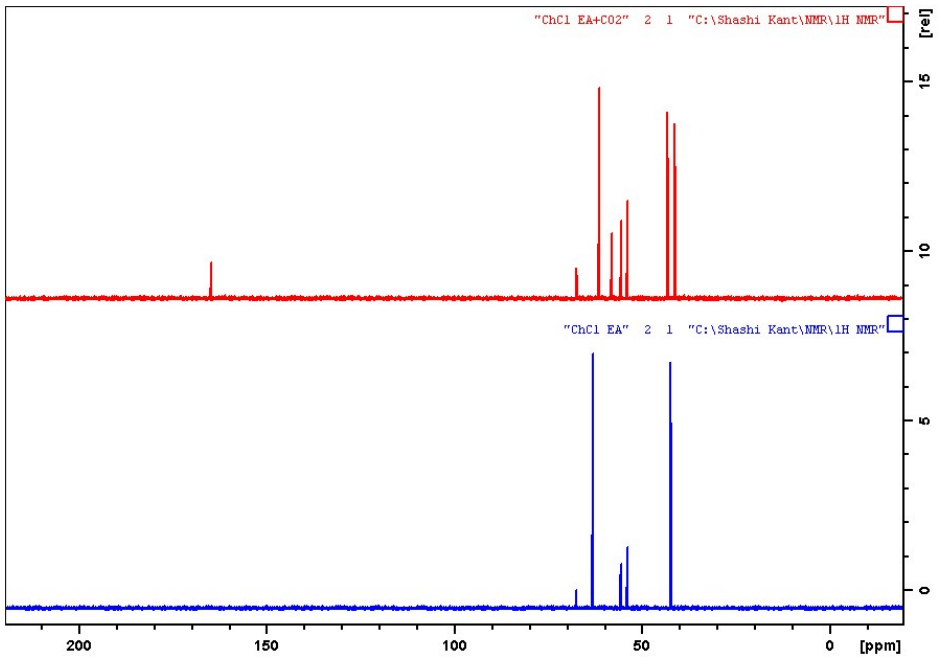


Fig S19. ^{13}C NMR spectra of [ChCl][EA] = 1:6 before (–) and after (–) CO_2 capture

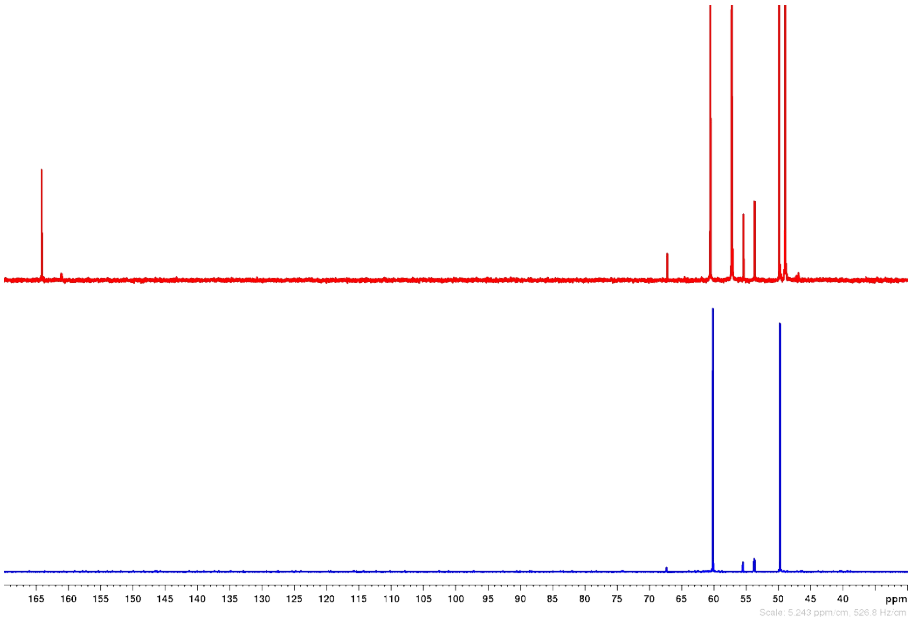


Fig S20. ^{13}C NMR spectra of [ChCl][DEA] = 1:12 before (–) and after (–) CO_2 capture

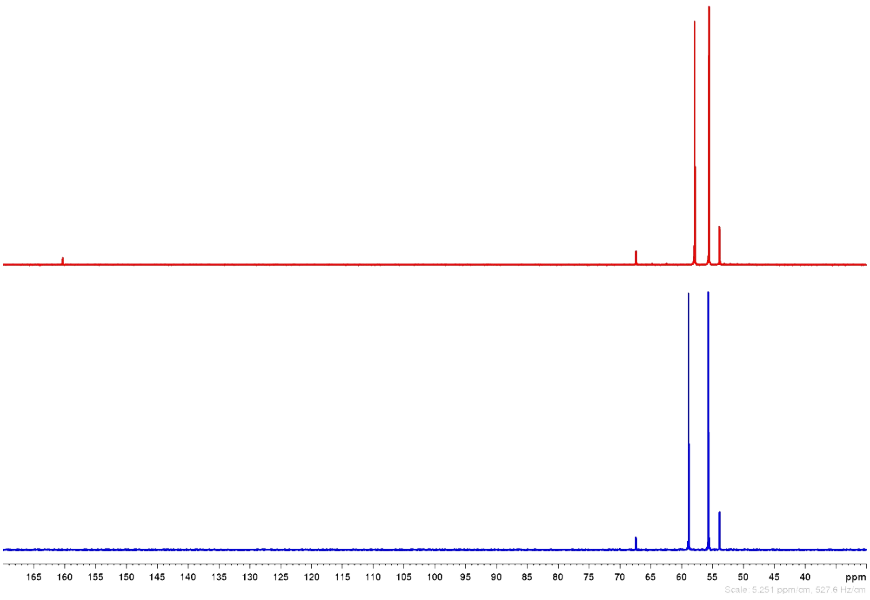


Fig S21. ^{13}C NMR spectra of [ChCl][TEA] = 1:3 before (–) and after (–) CO_2 capture

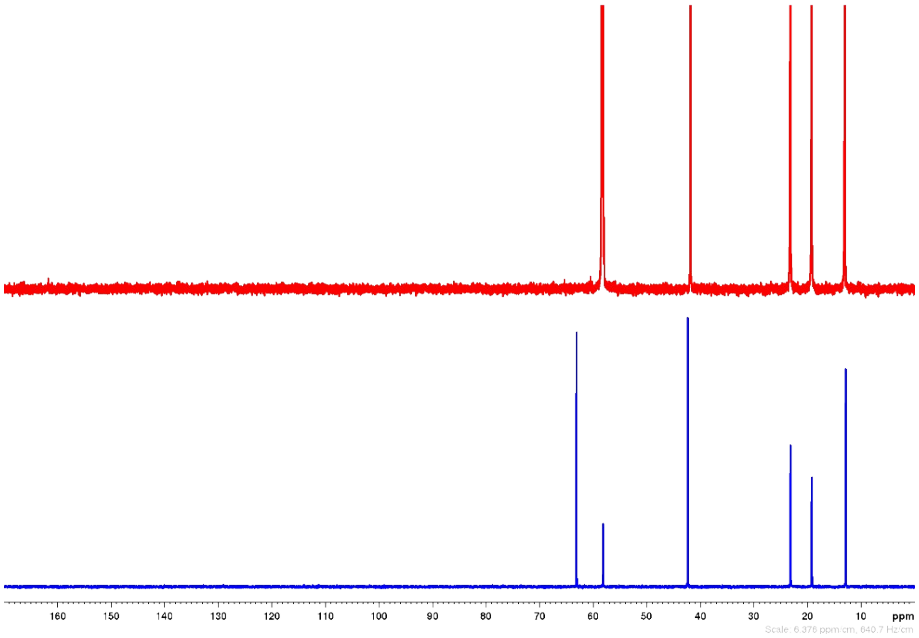


Fig S22. ^{13}C NMR spectra of [TBAB][EA] = 1:5 before (–) and after (–) CO_2 capture

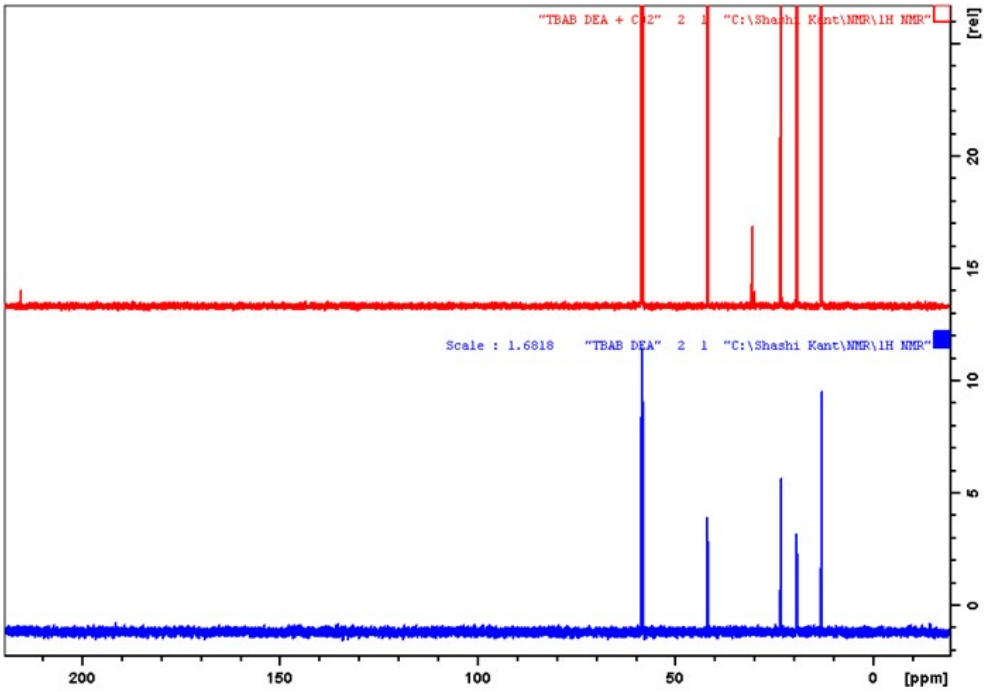


Fig S23. ^{13}C NMR spectra of [TBAB][DEA] = 1:2 before (–) and after (–) CO_2 capture

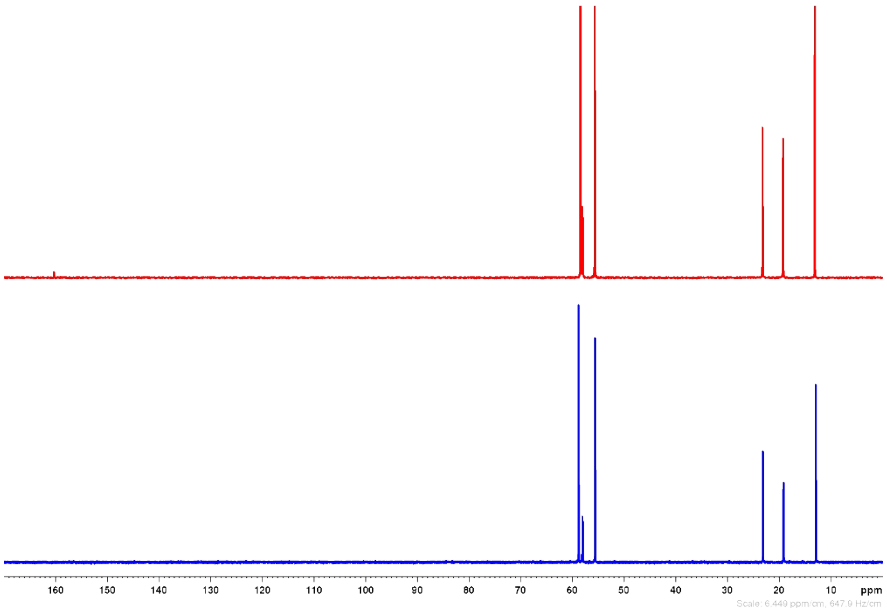


Fig S24. ^{13}C NMR spectra of [TBAB][TEA] = 1:2 before (–) and after (–) CO_2 capture

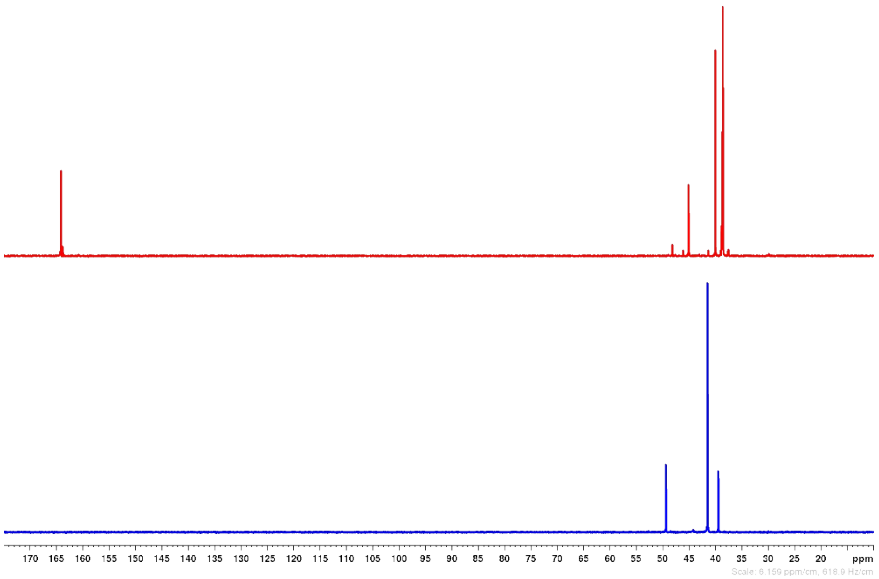


Fig S25. ^{13}C NMR spectra of [DETA.Cl][EDA] = 1:4 before (–) and after (–) CO_2 capture

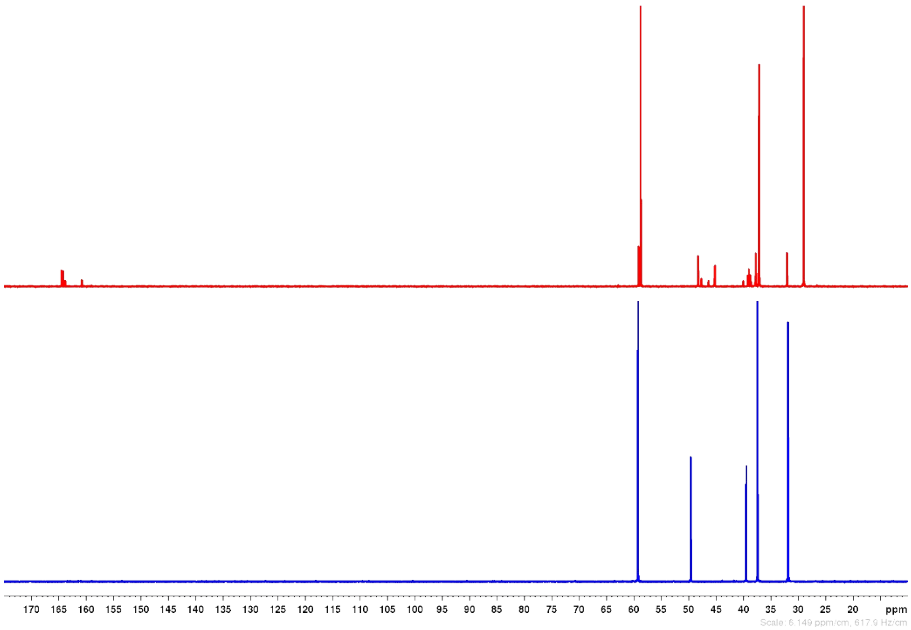


Fig S26. ^{13}C NMR spectra of [DETA.Cl][AP] = 1:4 before (–) and after (–) CO_2 capture

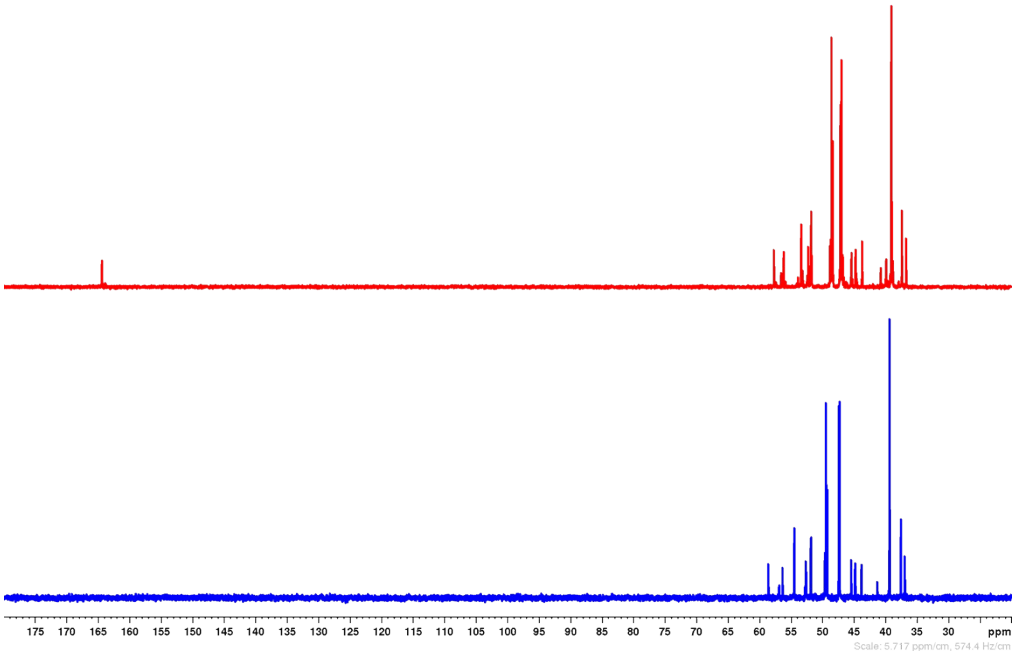
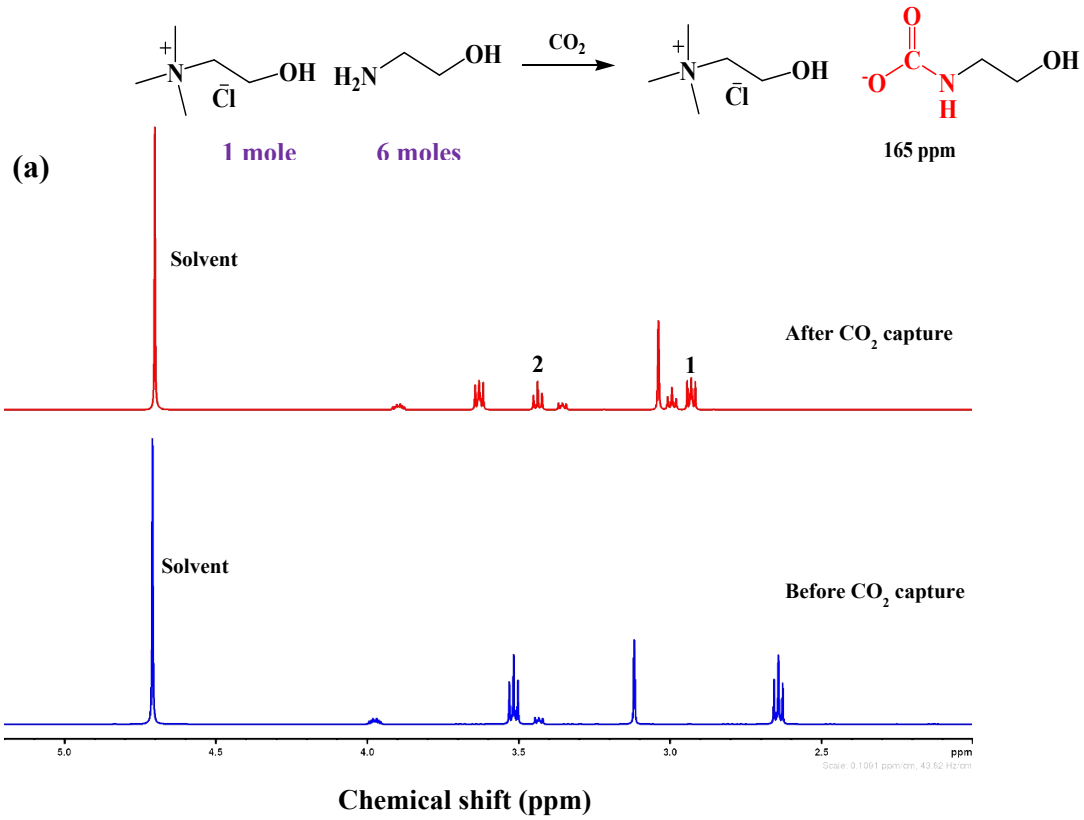


Fig S27. ^{13}C NMR spectra of [DETA.Cl][TEPA] = 1:4 before (–) and after (–) CO_2 capture

6. Anomalies in the ^{1}H and ^{13}C-NMR spectra of DESs before and after CO_2 capture

CO_2 absorption in all DESs was also monitored by recording the ^{13}C-NMR spectra before and after the CO_2 capture (Fig. S28). The ^{13}C NMR of DESs post CO_2 capture reveal the presence of the carbamate (NH_2COO^-) and carbonate/bicarbonate (CO_3^{2-}/HCO_3^-) signals in the spectrum at ~164 ppm and ~160 ppm, respectively. Surprisingly, for those DESs which were prepared beyond 1:2 HBA:HBD ratio, the number of ^{1}H- and ^{13}C-NMR signals exceeded those obtained for pure DESs after CO_2 intake (see Figs. S19 –S27). A typical case of [ChCl][EA] = 1:6 is shown in Fig. S28. The extra peaks in ^{1}H- and ^{13}C-NMR spectra are designated as 1 and 2, respectively.



(b)

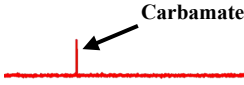
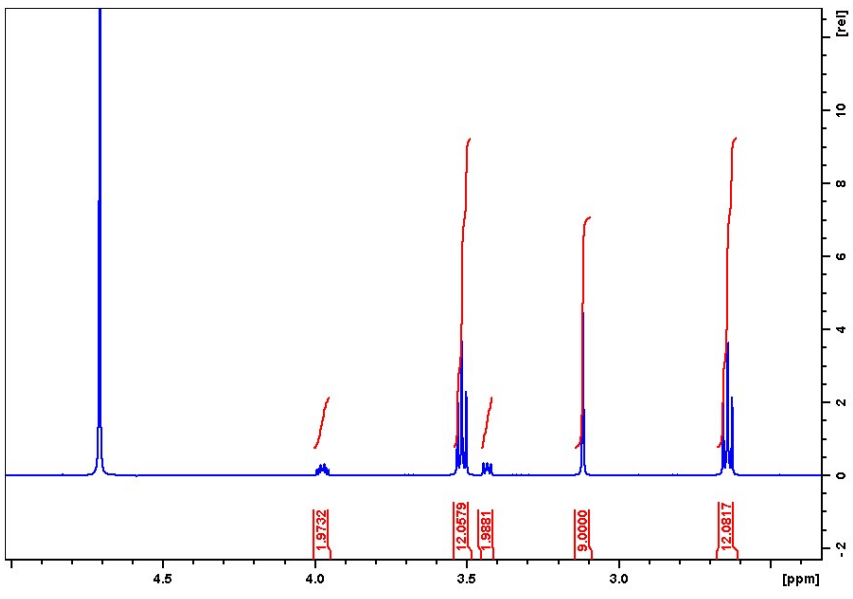


Fig S28. (a) ^{1}H- and (b) ^{13}C-NMR spectra of [ChCl][EA] = 1:6 before and after CO_2 capture.

The anomalies in the ^{1}H- and ^{13}C-NMR spectra of [ChCl][EA] = 1:6 post CO_2 capture arise due to the difference in the chemical shifts of the six moles of [EA] as suggested by the ^{1}H NMR and HSQC spectra of the DES (Figs. S28-S31). These spectra suggest that during the CO_2 capture only two moles of [EA] out of six moles participate in the binding with CO_2 and the remaining four moles remain unaffected of it and interact only with the HBA *i.e.* [ChCl]. This difference in the behaviour of [EA] results in the appearance of the new peaks in ^{1}H- and ^{13}C-NMR spectra, respectively. The molar uptake plot suggest a semimolar mechanism, where two moles of [EA] interacts with one mole of CO_2 (Fig. S32). The molar plot forfeits the observations drawn from the ^{1}H NMR and HSQC spectra.

NMR

1:6 before capture.



Integrated ^{1}H NMR spectra of [ChCl][EA] = 1:6 and after CO_2

Fig S29. Integrated ^{1}H NMR spectra of neat [ChCl][EA] = 1:6

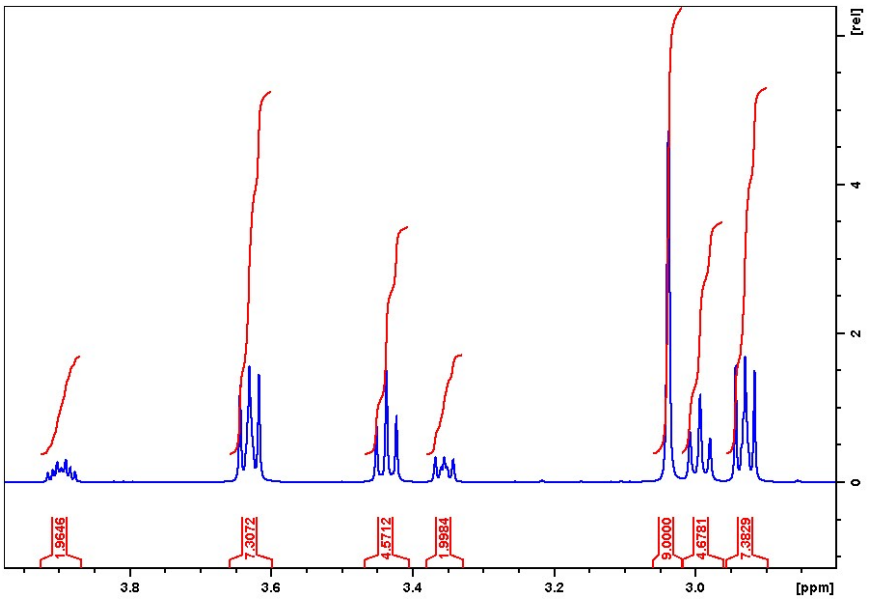


Fig S30. Integrated ^{1}H NMR spectra of [ChCl][EA] = 1:6 after CO_2 capture

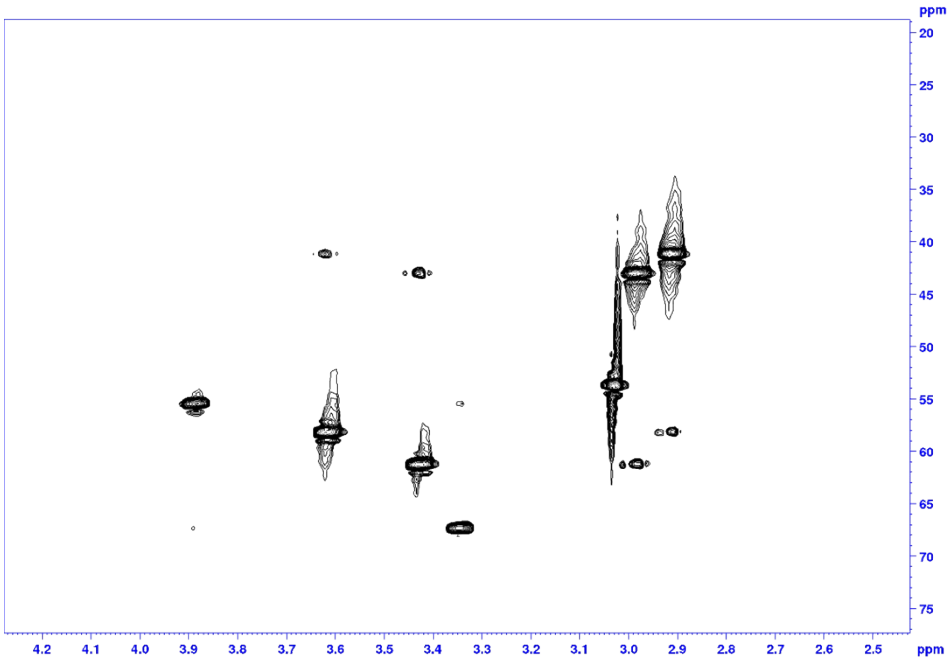


Fig S31. HSQC spectra of [ChCl][EA] = 1:6 post CO_2 capture

A typical molar uptake plot of CO_2 in DES

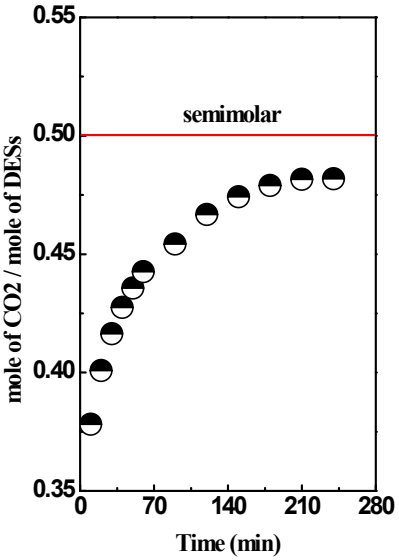
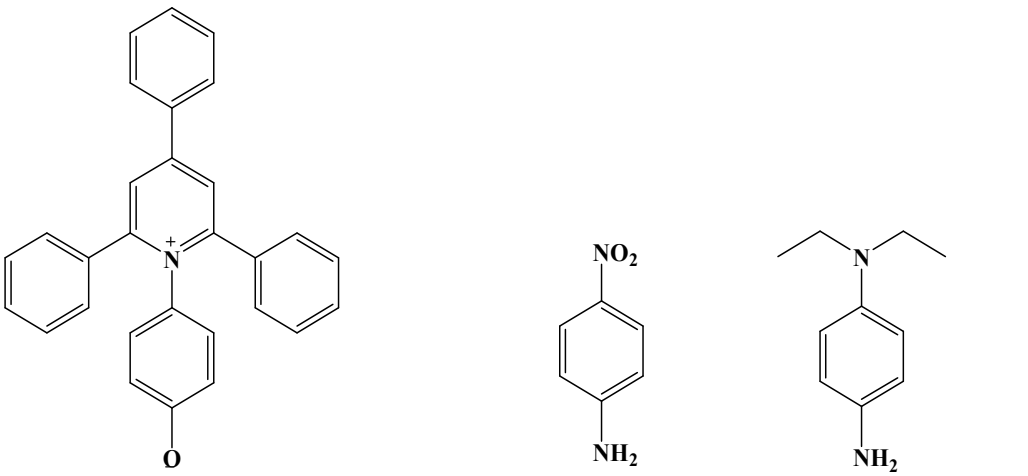


Fig S33. A typical semimolar CO_2 uptake plot.

7. Polarity determination, viscosity measurement, Hammett basicity measurement and CO_2 capture measurement

Polarity determination

A stock solution of 10^{-2} M in methanol for all solvatochromic dyes was used for the polarity measurements. The required amount of the stock solution was transferred in a glass vial first and methanol was removed subsequently by blowing nitrogen gas into the vial. To this, 1ml of DESs was added and the resultant solution was taken into a 1.3 ml quartz cuvette under nitrogen atmosphere and sealed with a septum and subjected to UV-visible spectrophotometer. The wavelength of maximum absorption (λ_{max}) was recorded at room temperature for different dyes in DESs and polarity parameters were derived by the empirical equations given in the results and discussion section.



2,6-diphenyl-4-(2,4,6-triphenyl-pyridinium-1-yl) phenolate (1) **4-nitroaniline (2)** ***N,N*-diethyl-4-nitroaniline (3)**

Figure S32. Structure of solvatochromic dyes.

The $E_T(30)$ measures the dipole-dipole interactions, hydrogen bond donor-acceptor forces and π-π interactions present in a medium and can be calculated from the lowest energy absorbance band maxima (λ_{max}^{abs}) of the betaine dye (30) by following equation 1.

$$E_T(30) = 28591.5 / \lambda_{max}^{abs} \text{ kcal mol}^{-1} \quad (1)$$

The polarity index (π^*) measures electrostatic strength between the probe and its cybotactic environment. A high π^* value indicates that the medium has higher electrostatic/bipolar interactions. The π^* was estimated based on the wavenumber of absorption maxima of *N,N*-diethyl-4-nitroanoline (kK), a non-hydrogen bond donor dye by the following expression,

$$\text{Polarity index } (\pi^*) = \nu_{(3)\,max} = 27.52\text{-}3.182\pi^* \quad (2)$$

The α measures the hydrogen bond donor strength of the solvent and was determined from the $E_T(30)$ and π^* according to equation 4.

$$\alpha = [E_T(30) - 14.6(\pi^* - 0.23) - 30.31]/16.5 \quad (3)$$

The β denotes the hydrogen bond acceptor strength of the solvent and was obtained because of the enhanced solvatochromic shift of 4-nitroaniline absorbance band relative to its homomorph *N,N*-diethyl-4-nitroaniline by the following expression.

$$\nu_{(2)max} = 1.035\nu_{(3)max} - 2.8\beta + 2.64 \quad (4)$$

Measurement of viscosity

The viscosity (η) of different DESs were measured at 298K by using a Brookfield rotating viscometer (RVDV1) with a cone and plate arrangement. The viscosity (η) values of DESs were obtained according to the given equation:

$$\eta = (100/RPM)(TK)(torque)(SMC)$$

where, TK (0.09373), RPM and SMC (0.327) are the viscometer torque constant, speed and spindle multiplier constant, respectively.

CO_2 absorption experiment

In the current work, CO_2 absorption measurements were carried out by bubbling CO_2 gas into a vial containing 3g of DES at a flow rate of 50 ml min^{-1} and recording the weight at a regular intervals. The differential weight of the absorbed CO_2 was used to calculate the gravimetric amount of absorbed CO_2. The electronic balance used for weighing had an accuracy of ± 0.1 mg.

Determination of Hammett basicity (H_-)

The Hammett basicity denotes the tendency of a basic solution to capture protons. In case of weak acids, it can be calculated by using the following equation,

$$H_- = pK(HI) + \log\left([I^-]/[HI]\right) \quad (5)$$

where, $pK(HI)$ is the ionization constant of indication in water, $[I^-]$ and $[HI]$ represents molar concentrations of anionic and neutral forms of indicator, respectively. A basic medium with a larger value of H_- will have higher basicity. The measurement of the H_- depends on the proper selection of the Hammett indicator. The commonly used indicators are 4-nitrobenzylcyanide, 4-nitrophenol and 2,5-dinitrophenol. The pK(HI) of these indicators are 13.43, 7.15 and 5.15, respectively. For the reliability of our measurements, we first measured the Hammett basicity of different w/w% of aqueous hydrazine solutions and compared them with the reported value (Table S1).[1] The accuracy of the H_- measurement depend on the complete conversion of indicator into anionic form.[2,3]

Table S1. Comparison of Hammett basicity for aqueous hydrazine solution

Solvents	H_- **(calculated)**	H_- **(reported)**
15% N_2H_2	11.77	11.93
20% N_2H_2	12.29	12.29
25% N_2H_2	12.64	12.72
30% N_2H_2	13.05	13.15

8. Table S2. $E_T(30)$ and π* polarity parameters for DESs

DESs	$E_T(30)$/kcal.mol^{-1}	π*
[ChCl][EA] = 1:6	49.6	1.10
[ChCl][DEA] = 1:12	50.0	0.97
[ChCl][TEA] = 1:3	51.1	1.02
[TBAB][EA] = 1:5	53.4	1.08
[TBAB][DEA] = 1:2	54.0	1.06
[TBAB][TEA] = 1:2	55.1	1.06
[DETA.Cl][EDA] = 1:4	58.7	1.32
[DETA.Cl][AP] = 1:4	60.1	1.17
[DETA.Cl][TEPA] = 1:4	53.2	1.18

9. Depiction of pseudo-first order rate constant

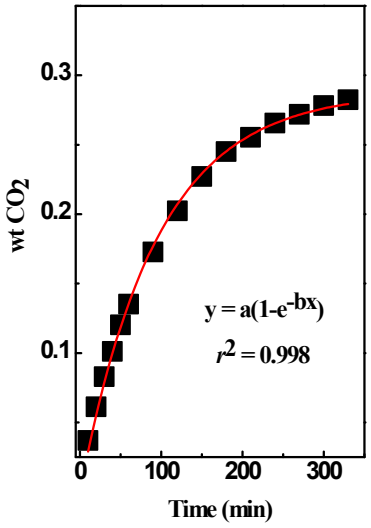


Figure S34. A representative plot of weight of absorbed CO_2 against time in a DES to derive pseudo 1st order rate constant (k).

10. Table S3. Table showing goodness of fit of the Box-Lucas equation in DESs

DESs	**R^2**
[TBAB][EA] = 1:5	0.83395
[TBAB][DEA] = 1:2	0.97892
[TBAB][TEA] = 1:2	0.97359
[ChCl][EA] = 1:6	0.85967
[ChCl][DEA] = 1:12	0.8572
[ChCl][TEA] = 1:3	0.99805
[DETA.Cl][EDA] = 1:4	0.93594
[DETA.Cl][AP] = 1:4	0.82838
[DETA.Cl][TEPA]= 1:4	0.94747

[1] N. C. Deno, *J. Am. Chem. Soc.*, 1952, **74**, 2039.

[2] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.

[3] R. J. Gillespie and T. E. Peel, *J. Am. Chem. Soc.*, 1973, **95**, 5173.