Supplementary Information

Experimental Methods

Synthetic Methods

DMEDAH formate (N,N-dimethylethylenediammonium formate, Figure 1a) was synthesised by slowly adding formic acid (3.5 g, 76 mmol) to N,N-dimethylethylenediamine (7.7 g, 76 mmol) contained in an ice bath with continuous stirring. The stoichiometry (1:1) of the acid–base reaction was confirmed by an aqueous titration method and samples of the prepared ILs were subsequently tested for correct pH after dilution into water (0.1 M). The equivalence point pH was determined to be 8.5. We have found this to be a sensitive, routine test of final stoichiometry for these materials. ^{13}C NMR: NMR (600 MHz): 36.68 ppm (H_3N^+-$\underline{C}H_2$), 45.25 ppm (($\underline{C}H_3)_2NCH_2$), 56.42 ppm ($(CH_3)_2N\underline{C}H_2$), 168.56 ppm ($H\underline{C}OOH$).

DMAPAH acetate ((3-dimethylamino)-1-propylammonium acetate, Figure 1b) was made in a similar manner as described for DMEDAH formate. Typically it is made by slowly adding acetic acid (3.7 g, 61 mmoles) to (3-dimethylamino)-1-propylamine (6.3 g, 61 mmoles) kept in an ice bath. The contents were continuously stirred till the addition was complete and the stoichiometry was confirmed by aqueous titration method. The equivalence point pH was determined to be 9.4. ^{13}C NMR (600 MHz):24.78 ppm ($H_3\underline{C}COO^-$),25.70 ppm (H_3N^+-CH_2-$\underline{C}H_2$-). 37.61 ppm (-CH_2-$\underline{C}H_2$-$N(CH_3)_2$), 45.16 ppm (CH_2-CH_2-$N(\underline{C}H_3)_2$), 56.67 ppm (H_3N^+-$\underline{C}H_2$-CH_2-), 176.65 ppm ($H_3C\underline{C}OO^-$).

DMPDAH *bis*(trifluoromethanesulfonyl)imide (NTf_2) was synthesized by the dropwise addition of an aqueous solution of trifluoromethanesulfonic acid (7.333g, 26.1) and (3-dimethylamino)-1-propylamine (2.667g, 26.1 mmol) at 0°C . Upon completion, the water was removed by rotary evapouration.

^{13}C Nuclear Magnetic Resonance Spectroscopy (^{13}C NMR)

Approximately 4 g of each PIL was placed in an open sample vial, which was placed in a sealed container with a constant CO_2 feed blowing through it, maintaining the CO_2 pressure at 1 atm. The samples were left for 4 hours under these conditions before being placed into E-type NMR tubes (Schott) and inserted into the instrument.^{13}C experiments were performed on a Bruker NMR (600 MHz, 14.1 T) at 20 °C using a standard pulse sequence with a relaxation time of 10 seconds. The samples were run without an internal standard due to the stability of the magnetic field generated in the instrument. Data was collected and analyzed using the Bruker Topspin software that comes with the instrument.

High Pressure CO_2 loading

Approximately 2 g of each PIL was placed in a glass vial and enclosed in a 100 mL capacity autoclave. The chamber was pressurized to 0.7 MPa with CO_2 gas (BOC, 99.9 %) and kept at 20 °C for 4 days. The atmosphere was regenerated to 0.7 MPa after 24 hours to maintain the pressure. After 4 days, samples were removed from the chamber and allowed to equilibrate to 1 atmosphere for 1 hour before spectra were obtained. Mass measurements confirm an increased CO2 load, however since the CO2 load is constantly being lost during handling for the spectroscopic experiments we cannot quantify the relevant CO2 content.

Spectroscopic Investigations

NMR

In order to probe the speciation of DMEDAH Formate and DMPDAH Acetate in the CO_2 loaded and unloaded states, ^{13}C NMR experiments were performed to gain an understanding of the species present (Figure S1 and Figure S2). Such methods have also been used with great success by Perinu *et al*.[21]. The samples used for NMR were held under a flowing stream of CO_2 at 1 atm for 4 hours prior to being loaded into NMR tubes.

The primary feature of interest in the spectra of both DMEDAH Formate (Figure S1) and DMPDAH Acetate (Figure S2) is the appearance of a distinct carbamate peak at around 162 ppm that is indicative of a carbamate functionality being formed in the PILs. The formation of a single carbamate peak also provides several useful tools for quantifying the amount of CO_2 taken up by the DMEDAH Formate sample. As no other peaks have formed in areas that would indicate the formation of bicarbonate (≈ 164 ppm) formed from any residual water or dissolved CO_2 (≈ 124 ppm), we can state that the carbamate mechanism is the primary mechanism of action. Integration of this peak against the two separate methyl peaks of DMEDAH (45 ppm) gives CO_2 mole uptake ratio of 0.34 ± 0.5, which is in good agreement with the 0.36 ± 0.5 as determined in the mass uptake experiments. For DMPDAH Acetate, this ratio was found to be 0.17 :1. This was expected since the fully loaded sample was too viscous to load into the NMR tube. Despite being unable to replicate the fully loaded PIL shown in the DSC experiments, these spectra confirm the carbamate uptake mechanism.

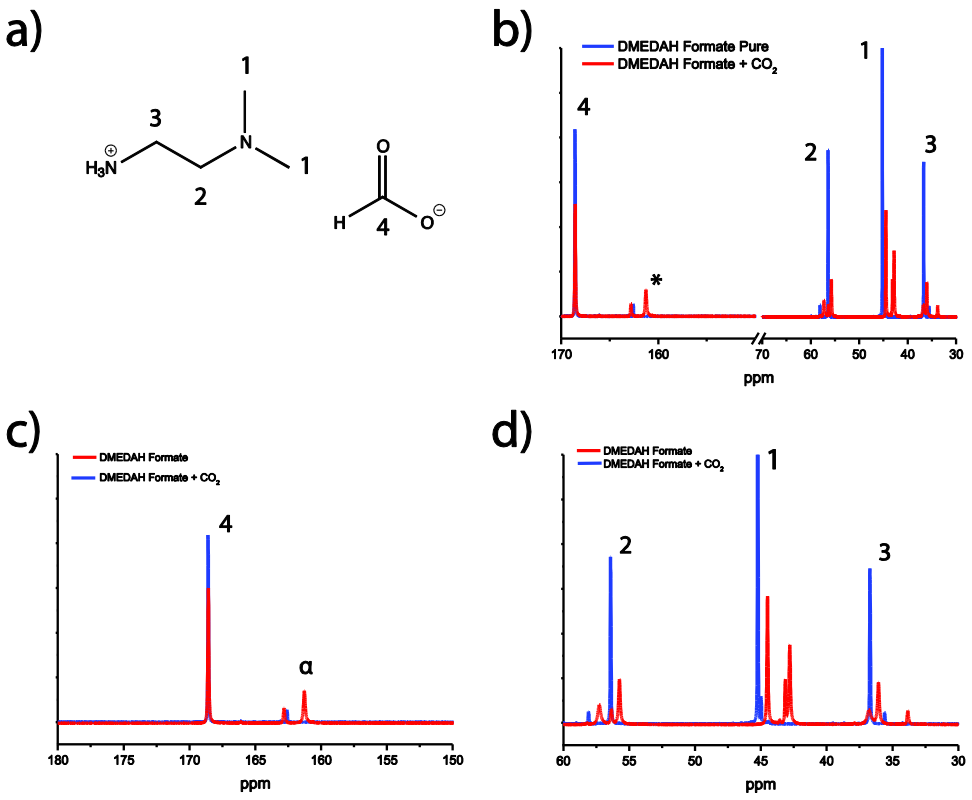

Figure S1: a) Molecular structure of DMEDAH Formate b) Full scale ^{13}C NMR of DMEDAH Formate in the unloaded (blue) and loaded (red) state with c) downfield spectra and d) upfield spectra.

In the spectra contained in Figure S1, it is clear that the DMEDAH Formate shows four ^{13}C peaks, 3 associated with the cation and a single carbonyl peak from the Formate anion, shown in Figure 5a. Several small peaks occur in the region of other peaks in the neat DMEDAH Formate sample, which we have attributed to either minor impurities, or various long-lifetime structural moieties that can cause a distinctly separate chemical environment. Regardless, the low intensity of these peaks indicates that they are of extremely low concentration and are unlikely to play any role in the capture of CO_2.

Upon the loading of the sample under a 1 atm CO_2 environment (red), several key changes can be observed in the various spectra (Figure S1 b-d). Firstly, a new peak occurs at approximately 162 ppm, which has been attributed to the carbamate ^{13}C environment formed during CO_2 capture (indicated by α)[20] Secondly, the three major peaks associated with the DMEDAH cation have been shifted downfield to around 56 ppm, 45 ppm & 36 ppm respectively and have also split to become two separate peaks, indicating two distinct chemical environments.

The formation of a single carbamate peak also provides several useful tools for quantifying the amount of CO_2 taken up by the DMEDAH Formate sample. As no other peaks have formed in areas that would indicate the formation of bicarbonate (≈ 164 ppm) or dissolved CO_2 (≈ 124 ppm), we can state that the carbamate mechanism is the primary mechanism of action. Integration of this peak against the two separate methyl peaks of DMEDAH (45 ppm) gives CO_2 mole uptake ratio of

0.34 ± 0.5, which is in good agreement with the 0.36 ± 0.5 as determined in the mass uptake experiments.

When the same experiment and methodology was performed on the DMPDAH Acetate system (Figure S2), the spectra show 6 carbon environments that have been assigned according to Figure S2 a.

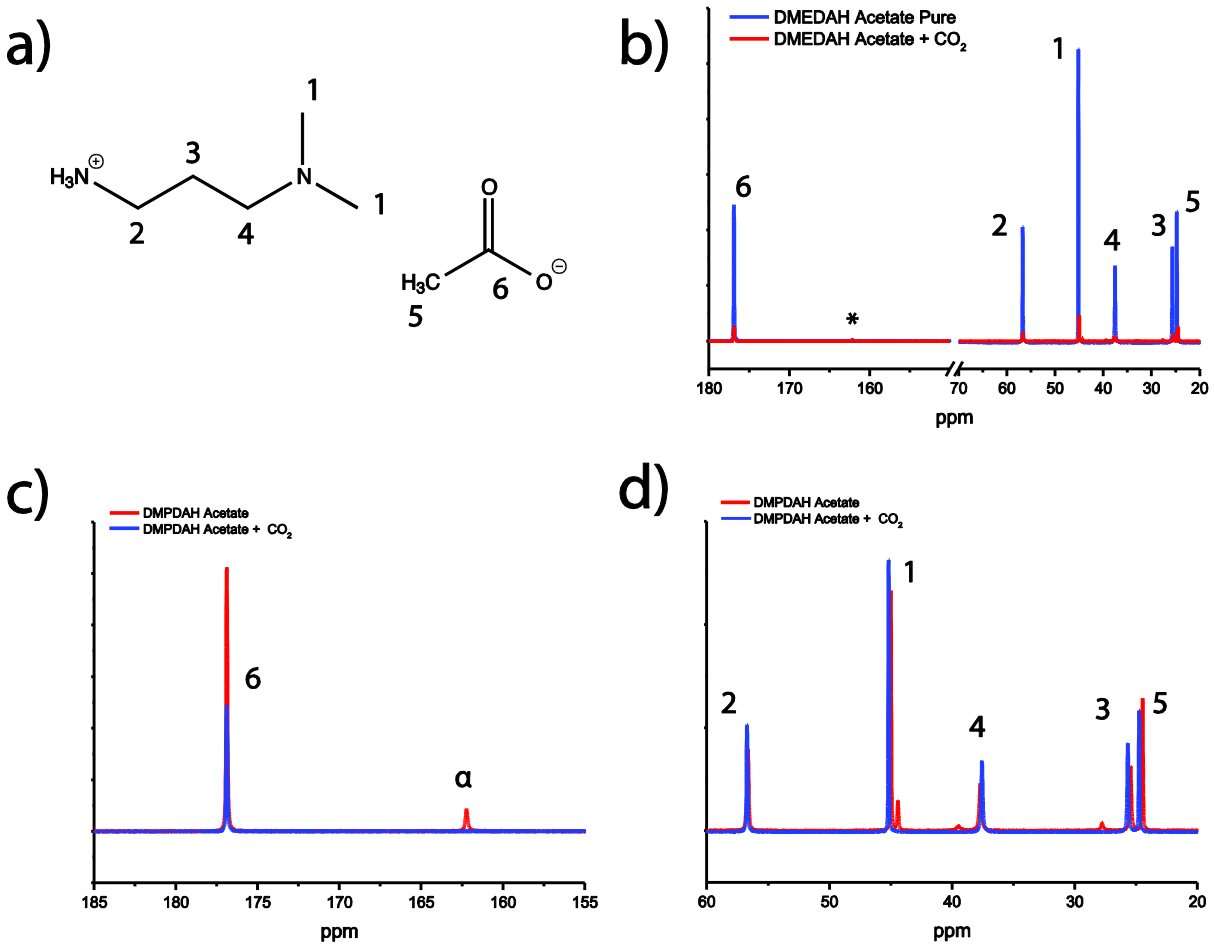

Figure S2: a) Molecular structure of DMPDAH Acetate b) Full scale ^{13}C NMR of DMPDAH Acetate in the unloaded (blue) and loaded (red) state with c) downfield spectra and d) upfield spectra.

Much like the DMEDAH Formate, the unloaded sample demonstrates a very clear spectrum with single peaks indicating the different ^{13}C environments. Upon addition of CO_2, we once again see the peak at 162 ppm (α) indicating a carbamate capture mechanism. However, unlike the DMEDAH Formate system, the level of peak splitting is lower. This may be in part due to the larger volume of the DMPDAH cation, but is most likely due to the apparently lower uptake of CO_2 in this experiment, as obtained by integrating the carbamate peak, showing a ratio of 0.17 :1. This was expected since the fully loaded sample was too viscous to load into the NMR tube. Despite being unable to replicate the fully loaded PIL shown in the DSC experiments, these spectra confirm the carbamate uptake mechanism.

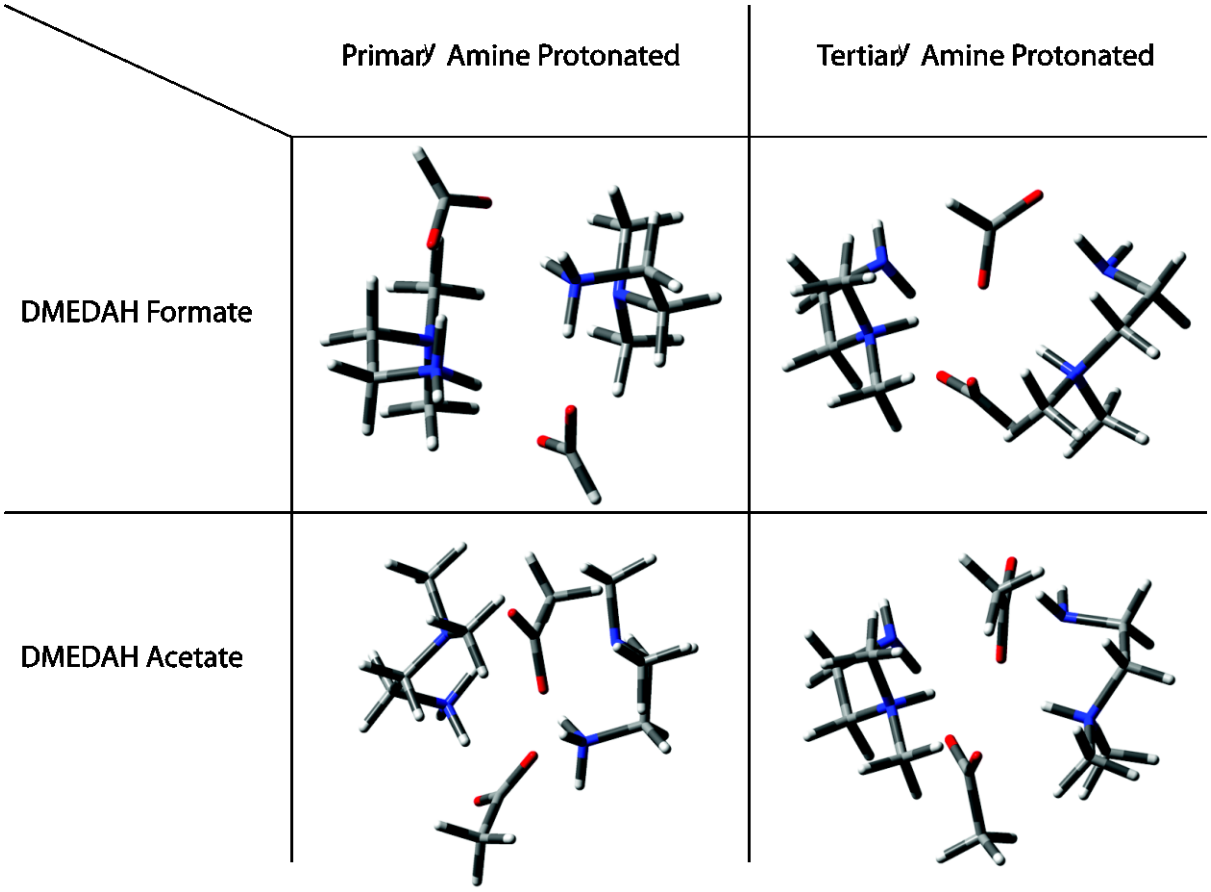

Figure S3: Calculated clusters of DMEDAH Formate and DMEDAH Acetate with protonation on either the primary or tertiary amine. Red: Oxygen, Blue: Nitrogen, Grey: Carbon, White: Hydrogen.

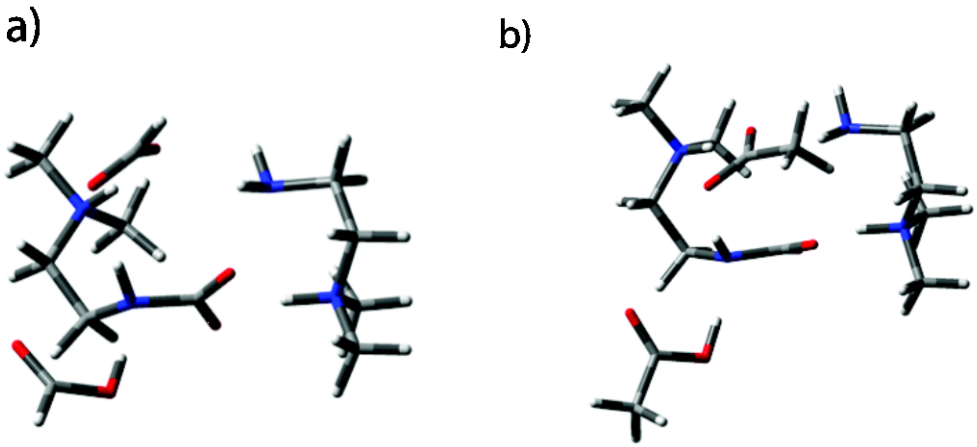

Figure S4: Molecular structure of the calculated cluster of a) DMEDAH Formate carbamate species and b) DMPDAH Acetate carbamate species . Red: Oxygen, Blue: Nitrogen, Grey: Carbon, White: Hydrogen.

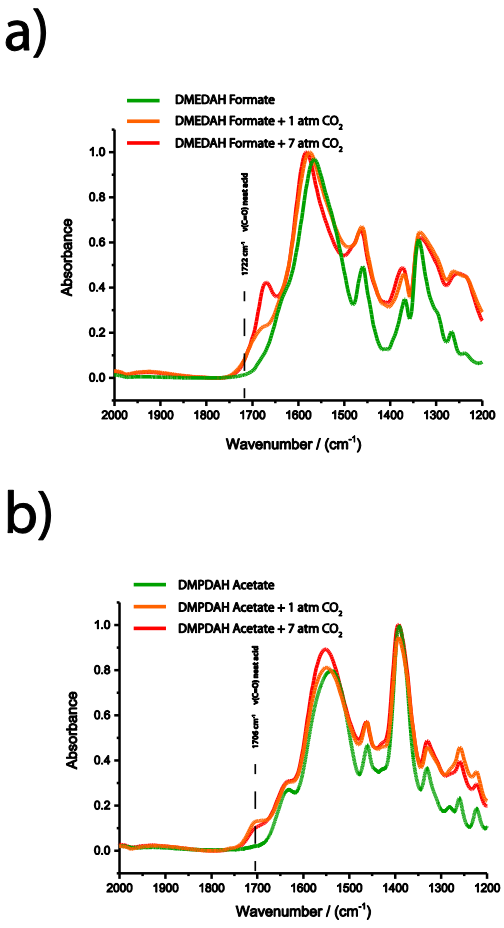

Figure S5: c) Experimental ATR-IR Spectra of DMEDAH Formate under different loading conditions d) Experimental ATR-IR Spectra of DMPDAH Acetate under different loading conditions.