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# Synergetic effects on the capture and release of CO<sub>2</sub> using guanidine and amidine superbases†

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The capture of CO<sub>2</sub> from air is of utmost importance, not only to reduce its impact on climate change but also for its utilisation as a tremendous, renewable source of C1 building blocks for sustainable chemical synthesis. Novel and known superbase structures are compared in a new selection of solvents for CO2 capture and release. Bicyclic amidine and quanidine superbases with 6-5, 6-6 and 6-7 configurations and many methylated analogues are investigated. As reported here, identified superbase/solvent combinations offer a highly efficient, reversible, and kinetically favourable CO2 capture process from air. The two most beneficial superbase/solvent synergic combinations identified are 1,5,7-triazabicyclo[4.3.0]non-6-ene (TBN) in butyl acetate and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in acetonitrile. They reach saturation after 15 min with pure CO<sub>2</sub> and after 24 hours under open-air conditions and release CO<sub>2</sub> with a CO<sub>2</sub>/superbase molar ratio of 0.41 and 0.25, respectively. Due to the favourable thermodynamics of the systems, quantitative CO<sub>2</sub> release for TBN and DBN occurs under mild conditions at 90 °C and 60 °C within 20 minutes. The required time for a complete absorption-desorption cycle for both TBN-butyl acetate and DBN-acetonitrile was only 48.5 and 38.5 minutes respectively. Superbase-solvent mixtures are recyclable and the system retains its initial CO<sub>2</sub> capturing capability after 5 cycles. As this apparently easy emerging system design allows the direct capture of CO<sub>2</sub> from air, it has potential for positive utilization on the global scale.

## Introduction

Carbon dioxide is an overly abundant greenhouse gas, particularly from industrial point sources such as petrochemical, iron

## Sustainability spotlight

Direct carbon dioxide (CO2) capture from air is not only imperative for addressing the escalating climate crisis, but it also holds significant potential to serve as a sustainable and cost-effective source of C1 building blocks for the chemical industry. This emerging technology represents a crucial step towards mitigating the adverse impacts of anthropogenic carbon emissions and fostering a more sustainable future. On the other hand, current technologies rely on calcium based adsorbents or aqueous alkanolamine which require high energy to recover the captured CO2 for industrial applications. With the aim of developing efficient CO2 capture and release at low energy, the use of amidines and guanidine is becoming an attractive alternative to other processes. Herein, we introduced not only the importance of the structure of the superbases (amidine or guanidine). but also the role of the solvent and its synergetic effects on both capture and release of CO2. The effect of solvent has not been deeply investigated and plays a dual role in the thermodynamics and kinetics of CO2 capture and release.

and steel manufacturing and the cement industry.<sup>1-5</sup> Reducing anthropogenic CO<sub>2</sub> emissions is an important step towards carbon neutrality but it is insufficient to reach the anticipated CO<sub>2</sub> negativity that will be required.<sup>6</sup> Direct CO<sub>2</sub> capture from air is not only necessary but it also has great potential to provide a clean source of renewable and low cost C1 building blocks for the chemical industry.<sup>7,8</sup> Contributing to added-value products such as urea and inorganic carbonates, innovative processing of methanol and dry reforming with methane to jet fuels have also attracted much recent interest.<sup>9-12</sup> CO<sub>2</sub> is also essential in industrial scale synthesis of cyclic carbonates, polycarbonates, non-isocyanate polyurethanes (NIPU), and salicylic acid.<sup>13-19</sup>

Different technologies have been developed to capture  $CO_2$  from different sources, whether this is direct air capture (DAC) or from point sources such as flue gas. <sup>20,21</sup> Inorganic sorbents have been used to capture  $CO_2$  using the calcium oxide-calcium carbonate loop. However, the recovery process is energy intensive, posing challenges to future use. <sup>22</sup>

With the importance of removing CO<sub>2</sub> from flue gases as well as from air, different capture technologies were developed with many pros and cons for each of these methods.<sup>23</sup>

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Based on the limitation of solid sorbents, amine in solvent becomes an attractive alternative, since the reaction of an amine with  $\mathrm{CO}_2$  is a fundamental interaction in chemistry. This interaction leads to the formation of stable ionic species such as carbamate or (bi)carbonate. Currently, the most used absorbents for  $\mathrm{CO}_2$  capture in industries are amine-based aqueous solutions such as monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA) and N-methyldiethanolamine (MDEA).  $^{2,24,25}$  These amines strongly bind  $\mathrm{CO}_2$ , and high temperatures are needed (130  $^{\circ}\mathrm{C}$ ) for its recovery. Due to the high heat capacity of the reaction medium, this step also requires significant amounts of energy.  $^{26}$  Additionally, these absorbents face severe challenges with the loss of organic amines due to high volatility and decomposition during regeneration.  $^{2,27,28}$ 

Ionic liquids have improved this system by improving thermal stability, lowering loss of solution through lower vapour pressure and by having tuneable polarity in the choice of ion pairs. The choice of ion pairs also allows control over other physical and chemical properties. However, negative ions for ionic liquids tend to be halogenated or toxic, meaning they have little chance of being scalable to the problem at hand.<sup>29</sup>

Bicyclic organic amine superbases, particularly amidines and guanidines, have gained attention as promising alternatives to conventional alkanolamine for the capture of CO<sub>2</sub>. First, Jessop *et al.* studied 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with hexanol to form a switchable ionic liquid, reaching a polarity like that of water.<sup>30–32</sup> They were also able to recover CO<sub>2</sub> by simply heating the solution.<sup>33</sup> Not only does this system show reversible capture of CO<sub>2</sub>, but their results show that the energy consumption of this system is 50% less than that of a water–MEA mixture.<sup>31</sup> When amidine or guanidine captures CO<sub>2</sub>, in the presence of water, a bicarbonate anion is formed over the carbamate zwitterion.<sup>34,35</sup> The carbamate zwitterion can allow for stabilising intramolecular hydrogen bonding to occur, whereas the bicarbonate exists as separate ions.<sup>36</sup> An example of this can be seen in Fig. 1.

Amidine and guanidine superbases were further studied with different alcohols and hexane revealing further possibilities for reversible capture of CO<sub>2</sub>.<sup>30,32,37–39</sup> A review thoroughly described the effect of alcohols, ionic liquids, and deep eutectic solvent on

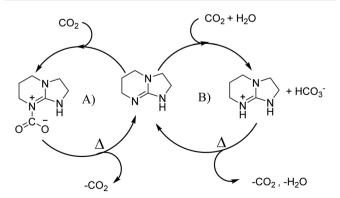


Fig. 1 Absorption schematic of  ${\rm CO_2}$  using TBN: (A) without water leading to the formation of zwitterions and (B) with the presence of water forming bicarbonate.

CO<sub>2</sub> capture.<sup>39</sup> On the other hand, the use of other organic solvents is not very well studied for CO<sub>2</sub> capture. Furthermore, fundamental understanding of the synergistic solvent effect with superbases is lacking and further improvement of the superbase (SB)–CO<sub>2</sub> capture system remains highly challenging.<sup>40</sup>

Herein we report highly reversible and kinetically favourable  $CO_2$  capture benefitting from the synergistic SB-solvent combinations. Even more strikingly, this concept also opens a window of opportunity to directly capture  $CO_2$  from air (DAC). The lowest temperature of  $CO_2$  release and which combinations release the most  $CO_2$  in a capture/release cycle would be considered optimal. As much as the structure of the SB is the core of reactivity, the selection of solvent is fundamental to attain maximum absorption and reversibility.

## Results and discussion

#### CO2 capture and release using different solvents

All in all, we evaluated 10 solvents and 8 superbases, totalling up to 80 combinations for the reversible capture of CO<sub>2</sub>. First, we saturated a 30% weight superbase solution with 15 min of bubbling pure CO<sub>2</sub> at room temperature (RT). To identify their reversibility capability in CO<sub>2</sub> capture, the release temperature and duration of CO2 released were studied (see the ESI†). Some solvents were excluded from further study as they, regardless of the superbase, demonstrated an irreversible binding of CO<sub>2</sub>, had limited solubility for the superbases or released CO2 above the boiling point of the solvent. We observed irreversible behaviour for example with TBU and toluene. Based on these observations, SB/solvent combinations demonstrated distinct differences for CO<sub>2</sub> release. While the structure of the superbase has a bearing on its ability to bind CO2, the synergetic effects with the solvent play an important role in both its absorption and release. Other physicochemical properties of the solvent, such as viscosity and polarity, also affect the mass transfer of CO<sub>2</sub> to the reaction medium. However, the literature regarding interaction of a solvent with a SB-CO<sub>2</sub> adduct is sparse, especially regarding its direct effect on the reversibility of the reaction.41

For further studies, we focused on five green solvents, ethanol, ethyl acetate, butyl acetate, propylene carbonate and acetonitrile.42,43 DBU was widely investigated and was used as a reference point to compare with 7 bicyclic amidines and guanidines consisting of different ring configurations; 6-5, 6-6 and 6-7. The amidines used in this study were DBU and 1,5diazabicyclo[4.3.0]non-5-ene (DBN). The guanidines studied 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), [1,5,7]triazabicyclo [4.5.0]-undec-5-ene (TBU) and 1,5,7-triazabicyclo [4.3.0]non-6-ene (TBN). Superbases were also compared with their N-methyl substituted analogues for their influence on binding  $CO_2$ ; 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (mTBD) and the racemic mixture of the isomers 7-methyl-1,5,7-triazabicyclo[4.3.0]non-5-ene (mTBN) and 5-methyl-1,5,7triazabicyclo[4.3.0]non-6-ene (mTBN) depending on whether the methyl group is on the 5 or 6 membered ring, respectively. 1,1,3,3-Tetramethylguanidine (TMG) was included as a representative of acyclic guanidines. The three major criteria for efficient systems are having a high molar ratio of  $\rm CO_2/SB$  released, low reversibility temperature and a rapid release.

In the selected aprotic solvents, the superbases reacted with pure  $CO_2$  and formed a white precipitate after 5 minutes. When heat is applied, any resulting slurries disappear, and  $CO_2$  gas is emitted. However, ethanol forms an ionic liquid, and so no precipitate is observed. There is a stark contrast in the SB- $CO_2$  adduct reversibility depending on the solvent used, including

two exceptions, TBN/ethyl acetate and TBN/acetonitrile being irreversible (see Tables S2 and S3 in the ESI†).

Compared to acyclic TMG, a bicyclic configuration increases electron density at the sp<sub>2</sub>-hybridised nitrogen, which increases its nucleophilicity and thus binding strength with CO<sub>2</sub>. From the series of bicyclic superbases, DBN/acetonitrile and TBN/butyl acetate are the best candidates when combining time, temperature and molar ratio of CO<sub>2</sub> bound and released. Based

Table 1 Selected superbase/solvent combinations and their properties towards the three major criteria: temperatures, time and the amount of released  $CO_2^a$ 

Superbase structure	Solvent	Temperature of CO <sub>2</sub> release (°C)	Time <sup>a</sup> (min)	Molar ratio CO <sub>2</sub> /SB
N N N TBN	Butyl acetate	90	20.5	0.41 (±6%)
DBN	Acetonitrile	60	20.5	0.25 (±3%)
TBU <sup>b</sup>	Acetonitrile	60	39	$0.25^b$
N N N mTBN	Acetonitrile	60	25	0.16 (±4%)
N N H TBD	Acetonitrile	65	29	0.13 (±6%)
DBU	Ethanol	60	17	0.13 (±6%)
N N N MTBD	Butyl acetate	65	26	$0.05~(\pm4\%)$
NH N N TMG	Ethyl acetate	60	32	0.11 (±6%)

<sup>&</sup>lt;sup>a</sup> The CO<sub>2</sub> absorption studies used 30 g of a superbase–solvent solution, with a 30% wt superbase. CO<sub>2</sub> was sparged through the solution for 30 minutes under vigorous stirring. The flask was then placed in a preheated oil bath at the selected temperature. The volume of CO<sub>2</sub> released was measured by using a burette system, and accordingly, the amount of CO<sub>2</sub> released and molar ratio of CO<sub>2</sub>/superbase were calculated. <sup>b</sup> Solubility issues in all selected solvents as TBU partially precipitates out of the solution after releasing CO<sub>2</sub>.

on results in Table 1, TBN and DBN, both having 6-5 heterocyclic ring configurations, are markedly faster in  $CO_2$  release than bicyclic amidines and guanidines with 6-6 and 6-7 ring combinations, including classical DBU. The other obvious benefit of TBN and DBN superbases is a higher molar ratio of superbase to  $CO_2$  (Table 1).

The structure of the superbase has a bearing on its ability to reversibly bind CO<sub>2</sub>. In the same solvent, the change from an amidine structure to its guanidine analogue increases the amount of reversibly released CO<sub>2</sub> (see the ESI, Table S3†). Despite similar reversibility temperatures, (when considering differences in solvent) non-methylated guanidines capture more CO<sub>2</sub> compared to their methylated analogues (TBD  $\nu$ s. mTBD). Having a H-bond donor and acceptor nitrogen in near proximity in a planar configuration, bicyclic guanidines are considered to bind CO<sub>2</sub> stronger than the corresponding amidines. Accordingly, we suggest that the *N*-methylation of TBD and TBN annihilates the intramolecular hydrogen bonding, and the desired zwitterionic SB-CO<sub>2</sub> interaction is remarkably decreased. This can be seen by their marked reduction in CO<sub>2</sub> adsorption compared to the non-methylated versions (Table 1).

To demonstrate reversibility even under moist conditions including atmospheric humidity, bicarbonate formation was forced by adding 1 mL of water to TBN and DBN in their respective reaction medium. Although the amount of precipitate increased significantly, the  $CO_2/SB$  ratio remained consistent showing no distinct effect on the reversibility and temperature needed (see Table S4†).

As shown above, besides the structure of the SB as the core of reactivity, the solvent choice becomes critical for efficient  $CO_2$  capture and release (Tables 1, S2 and S3 in the ESI†). Based on our observations, polar media are beneficial for  $CO_2$  binding to a certain extent as, depending on the SB structure, this can stabilise the SB- $CO_2$  adduct but at the same time, this can inhibit reversibility. This solvent effect is clearly illustrated with TBN; the reversibility is lost in acetonitrile, while in butyl acetate the capacity to absorb and release  $CO_2$  is among the best in this study (ESI, Tables S2 and S3†). To gain further insights into this phenomenon and the effect of solvent on the reversibility, we performed DFT calculations to determine the energetics.

#### **DFT** calculations

The present computational approach provides reasonably accurate Gibbs free energy data for the interaction of SB molecules with CO<sub>2</sub>; however, other important processes involved in CO<sub>2</sub> capture/release (CO<sub>2</sub> transfer from the gas to the solvent phase, diffusion, and precipitation) are not considered in our models. For this reason, the computed energetics can only be used in qualitative terms to interpret the observed trends.

To develop our understanding of the factors that determine the reversibility of the examined  $\mathrm{CO}_2$  capture/release processes, we investigated the interaction of SB molecules with  $\mathrm{CO}_2$  computationally. We considered three different  $\mathrm{SB/CO}_2$  systems (SB = DBN, TBN and mTBN) using acetonitrile and butyl acetate as solvent media (see Fig. 2). The applied computational protocol involved solution phase geometry optimizations

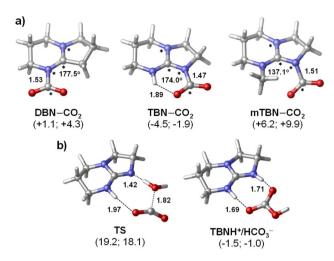


Fig. 2 Computed energetics of (a) adduct formation between superbases and  $CO_2$ ; and (b)  $HCO_3^-$  formation *via* the reaction of TBN with  $CO_2$  and  $H_2O$ . Relative Gibbs free energies computed in acetonitrile and butyl acetate are shown in parentheses (in kcal  $mol^{-1}$ ; with respect to separated reactants). Structures correspond to those optimized in acetonitrile. Selected bond lengths are in Å; dihedral angles defined by the atoms marked with asterisks are in degrees.

carried out at the  $\omega$ B97X-D/6-311G(d,p) level of DFT, where the solvent effects were incorporated *via* the implicit SMD solvation model. <sup>45,46</sup> Additional single-point electronic energy calculations were carried out using the LNO-CCSD(T)/CBS method to provide accurate energetics for the interaction of SB molecules with CO<sub>2</sub>. <sup>47,48</sup> The reported energy data refer to solution phase Gibbs free energies under standard conditions (T = 298.15 K and  $C = 1 \text{ mol L}^{-1}$ ). For further details, see the ESI.†

The barriers of SB-CO<sub>2</sub> adduct formation are predicted to be fairly low ( $\Delta G^{\ddagger} = 8-14 \text{ kcal mol}^{-1}$ ) suggesting that the rate of CO<sub>2</sub> capture is likely diffusion controlled. The thermodynamic stability data computed for the three zwitterionic SB-CO2 adducts (Fig. 2a) show a notable variation with the superbase molecule and with the solvent as well. Although the basicities of the three SB molecules as quantified by using the computed solution phase proton affinities are very similar (they are within 1.3 kcal mol<sup>-1</sup> for both solvents), the stabilities of the SB-CO<sub>2</sub> adducts vary in a much broader energy window (>10 kcal mol<sup>-1</sup>). In both solvents, TBN-CO<sub>2</sub> is predicted to be the most stable adduct followed by DBN-CO2 and mTBN-CO2 in the stability order. As expected, adduct formation is found to be more favoured thermodynamically in acetonitrile (by about 3 kcal mol<sup>-1</sup>) with all the three bases, since it is significantly more polar than butyl acetate (dielectric constants are 35.7 and 4.62, respectively).

The enhanced stability of TBN-CO<sub>2</sub> is associated with the intramolecular H-bonding interaction, which is absent in the other two adducts.<sup>36</sup> On the other hand, the *N*-methyl substituent in mTBN induces steric hindrance for the ideal planar arrangement of the guanidine-CO<sub>2</sub> unit in the adduct that would allow extended charge delocalization. Consequently, mTBN-CO<sub>2</sub> is predicted to be the least favoured zwitterionic species in the series. The distorted structure of mTBN-CO<sub>2</sub> is apparent in Fig. 2a (the highlighted NCNC dihedral angle deviates significantly from 180°). The adduct formation is

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nearly neutral thermodynamically for DBN/acetonitrile and TBN/butvl acetate combinations  $(\Delta G$ = +1.1 -1.9 kcal mol<sup>-1</sup>), which is in accordance with our observations in the CO<sub>2</sub> capture/release experiments that these are the two most efficient systems (Table 1). For the mTBN/CO<sub>2</sub> system, computations show slightly higher endergonicity even in acetonitrile ( $\Delta G = +6.2 \text{ kcal mol}^{-1}$ ), but this is likely compensated by the precipitation of the zwitterionic adduct species. The presented Gibbs free energies of adduct formation by no means can be regarded as a quantitative measure of the reversibility of CO2 capture; however, the computed trend accounts well for the observations.

The reaction of TBN and CO<sub>2</sub> in the presence of water was investigated computationally as well (Fig. 2b). The results suggest that the formation of the TBNH<sup>+</sup>/HCO<sub>3</sub><sup>-</sup> guanidiumbicarbonate ion pair in butyl acetate is also kinetically feasible at room temperature ( $\Delta G^{\ddagger} = 18.1 \text{ kcal mol}^{-1}$ ), although the computed barrier points to a slower process as compared to that of TBN-CO<sub>2</sub> formation (8.9 kcal mol<sup>-1</sup>). The overall reaction with water is predicted to be slightly less favoured thermodynamically ( $\Delta G = -1.0 \text{ kcal mol}^{-1}$ ) implying that this reaction will not affect the reversibility of CO<sub>2</sub> capture with TBN.

#### Design of experiment

Higher temperatures and higher concentrations are not guaranteed to increase efficiency, and as such it is important to create a simple model for the system.49 A design of experiment model was created and followed to cover TBN in butyl acetate (Fig. 3). The three variables covered were concentration of SB, temperature used to release CO<sub>2</sub> and length of exposure time to CO<sub>2</sub> for absorption. The results further evidence that higher temperatures do increase the speed and amount of CO<sub>2</sub> recovered, as does longer exposure time to CO<sub>2</sub>. It can also be observed that lower concentrations of SB allow for higher ratios of CO<sub>2</sub> to be captured. This further illustrates the mass transfer issue that affects the system.

#### **Kinetics**

The required time for the absorption for CO<sub>2</sub> to reach saturation was measured for TBN-butyl acetate and DBN-acetonitrile and compared with that of MEA in water as a reference (Fig. 4).

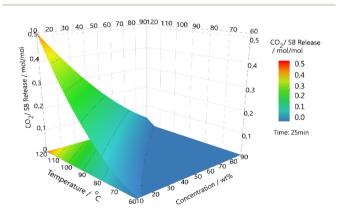


Fig. 3 Design of experiment surface plot of TBN in butyl acetate after 25 minutes of CO2 exposure.

Fig. 4 Absorption time of DBN, TBN and MEA in their respective solvents. Reaction conditions: TBN (30% wt) in butyl acetate, DBN (30% wt) in acetonitrile and MEA (30% wt) in water, at room temperature.

The required time for TBN-butyl acetate as well as DBNacetonitrile to reach saturation is only 15 min, compared to MEA in water which required more than 4 h. For DBN, the cycle for the capture and release of CO2 takes only 38.8 minutes compared to that of other systems which require much longer times per cycle.50,51

From the data reported in Table 1 and Fig. 4, it was possible to determine the yield of CO<sub>2</sub> recovery per cycle of absorption and release for the best superbase solvent combination (equation in the ESI†). For the absorption, the CO<sub>2</sub>-SB molar ratio for TBN-butyl acetate reached 0.49 and 0.42 for DBN-acetonitrile. For the release, the yield of CO2 recovery for TBN-butyl acetate and DBN-acetonitrile are 83.6% and 59.5% respectively showing that not all carbon dioxide was fully recovered.

#### Reusability

An important criterion for CO<sub>2</sub> capture is the reusability of the SB-solvent system for multiple cycles. For this reason, the reusability for both TBN and DBN systems was investigated for five consecutive capture/release cycles (Fig. 5).

After the sequence of 5 cycles, these two systems do not show any decrease in CO<sub>2</sub> capture/release capacity. Also, the five cycles required only tens of minutes compared to hundreds of minutes when other systems were used, showing the better efficiency of our system.52,53

#### CO2 capture from air

To continue our experimental investigations, we examined the two best candidates also for DAC. Due to low concentration of atmospheric CO2, saturation of the systems required 24 hours under ambient conditions. The quantitative release occurs, as in the case of pure CO2, at 60 °C and in less than 20 min for DBN. The DFT calculations corroborate our experimental results; reversal occurs regardless of if the CO2 adduct is in the carbamate or bicarbonate form. The required transition state energy for the release is nearly the same in the range of 9.3 to 12 kcal mol<sup>-1</sup>. Although the amount of CO<sub>2</sub> captured is 1/8 of

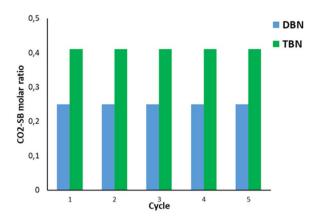


Fig. 5 Five consecutive recycling experiments with (a) TBN in butyl acetate (green) and (b) DBN in acetonitrile (blue).

the amount captured with pure CO<sub>2</sub>, this full reversibility, low energy requirement, and fast kinetics makes the system highly intriguing for DAC.

#### General considerations and sensitivity of the parameters

In this study, the focus was to investigate the application of superbases with organic solvents for direct air capture. For this reason, parameters employed in this study were at standard pressure and temperature. However, these parameters can influence the absorption and release of carbon dioxide. First, the concentration of CO<sub>2</sub> will play a dramatic role in the kinetics of absorption. By lowering the concentration from pure CO2 to the 400 ppm level, the time required to reach saturation will obviously be much longer going from few minutes to hours. As for the temperature, it is anticipated that a higher temperature will decrease the absorption capacity of the superbase solvent mixture. Another important parameter is the humidity from air which varies in different places around the world. The two systems presented are shown to be moisture tolerant for 5 cycles and can both release the captured CO2 regardless of if it is a carbamate or a bicarbonate. On the other hand, these systems will be tested for multiple cycles and moisture might induce degradation of the superbases.<sup>54</sup> If degradation by the presence of water is observed, to maintain constant activity, dry air should be favoured. These parameters will be further investigated in future studies during scale up development.

In comparison to MEA, our systems demonstrate lower corrosion and temperature of release, as well as faster absorption and desorption regardless of bicarbonate or carbamate ion formation. For industries this process is expected to have a low energy cost. As this apparently easy emerging system design allows the direct capture of CO<sub>2</sub> from air, it has potential for positive utilisation on the global scale.

#### Conclusion

In summary, we have established that bicyclic 6–5 ring configurations capture  $CO_2$  more efficiently than 6–6 and 6–7 configurations. TBN in butyl acetate and DBN in acetonitrile are shown to be the best systems of those in this study. The solvent

choice is important as it affects the reversibility and capture of CO<sub>2</sub>, either aiding capture or impeding CO<sub>2</sub> release. DFT calculations show that both the capture and the release of CO<sub>2</sub> are thermodynamically favourable for TBN in butyl acetate, which is the best system studied regardless of if it forms a zwitterion or a bicarbonate molecular adduct. The reversibility of TBN and DBN shows that capture-release of CO<sub>2</sub> can be performed for 5 cycles without losing the absorption capacity.

Future studies will consider prolonged repeatability experiments to account for stability, and degradation from moisture as part of the scale-up considerations. For flue gas applications,  $NO_x$  and  $SO_x$  durability would also need to be considered.

## Conflicts of interest

The authors declare no competing financial interest.

## Acknowledgements

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