## Reversible, solid state capture of carbon dioxide by hydroxylated amidines<sup>†</sup>

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## Hydroxylated amidine derivatives can capture, store, and release $CO_2$ reversibly in the solid state in a quantitative manner under clean and dry conditions at ambient temperature.

Energy-efficient  $CO_2$  absorbents are required for capturing  $CO_2$  emitted into indoor or outdoor environments and also for its storage and reutilization as a carbon resource.<sup>1–3</sup> Aqueous solutions of alkanolamines are the most commonly employed chemical  $CO_2$  absorption systems. However, the use of aqueous amine solutions has several disadvantages including high energy consumption due to the high specific heat of water and the generation of corrosive vapors.<sup>1,3</sup> Many studies have focused on the development of dry amine absorbents to avoid these disadvantages of aqueous solutions.<sup>4–8</sup>

Of the various amine types used in  $CO_2$  capture, amidine compounds react with  $CO_2$  in the presence of an alcohol to produce alkylcarbonate salts in the form of a trimolecular complex consisting of amidine,  $CO_2$ , and the alcohol in a 1:1:1 ratio.<sup>9–11</sup> The high nucleophilicity and stabilization of cationic species that result from delocalization in the amidine moiety enable their complexation with  $CO_2$  and the alcohol at room temperature. The resulting amidinium alkylcarbonate salts contain less hydrogen bonding than the carbamate or bicarbonate salts of other amines, so they decompose to equimolar amounts of amidine,  $CO_2$ , and the alcohol at relatively low temperatures.<sup>12</sup> It should therefore be possible to develop new materials for  $CO_2$  capture and storage by exploiting the unique nonaqueous, quantitative, and low temperature carbonation characteristics of amidines.

Endo *et al.*<sup>13,14</sup> reported that solid polymers containing amidine moieties in their side chains could capture  $CO_2$  under atmospheric pressure. Although the materials could trap  $CO_2$  without supplying water, the presence of a sufficient amount of water or alcohol is likely to facilitate the amidine– $CO_2$  complexation to enhance the capability of  $CO_2$  capture.

Here we report new hydroxylated amidine (HAM) derivatives that can capture and store  $CO_2$  in a quantitative manner under clean conditions. We synthesized three hydroxyalkylamidines, each of which contain equal numbers of amidine and hydroxyl groups that can react with an equimolar amount of  $CO_2$  with no additional protic solvents. In particular, HAMs with a

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<sup>†</sup> Electronic supplementary information (ESI) available: Experimental section, <sup>1</sup>H and <sup>13</sup>C NMR, HMQC and FT-IR spectra of the HAMs and the HAM-CO<sub>2</sub> salts. TGA of HAM/silica mixtures with various HAM contents. See DOI: 10.1039/b921688j

relatively large molecular mass are expected to capture or release  $CO_2$  in the solid state. The HAM- $CO_2$  salts can be stored at ambient temperature and pressure and are expected to generate pure  $CO_2$  gas after brief heat treatment.

The HAMs were synthesized via lithiation of the aliphatic bicyclic amidines 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) followed by reaction with epoxides (see the ESI<sup>†</sup>). Combining the amidine moiety with an alcoholic moiety effectively reduces the volatility of these compounds. In principle, the reaction of the lithiated amidines with stoichiometric equivalents of a molecule with multiple epoxy groups will result in the corresponding polymeric amidines with multiple hydroxyl groups. In this study, we synthesized mono- and dihydroxyalkylamidines, which are designated as DBUOH, (DBUOH)<sub>2</sub>, and (DBNOH)<sub>2</sub>, as shown in Fig. 1. Whereas DBUOH was a liquid, (DBUOH)2 and (DBNOH)2 were obtained as crystalline solids which melt near 116 and 149 °C, respectively. The HAM compounds do indeed react with equimolar amounts of  $CO_2$  in the absence of any protic solvent (Fig. 1b). DBUOH-CO<sub>2</sub>, the carbonated salt of DBUOH, was obtained as a white solid by directly bubbling anhydrous CO<sub>2</sub> gas into DBUOH. The carbonate salts of the other two HAMs as well as DBUOH were conveniently obtained as powders by bubbling CO<sub>2</sub> gas into their THF solutions followed by filtration of the precipitates. The structures of the three HAMs and the corresponding alkylcarbonate salts were confirmed by examination of their <sup>1</sup>H and <sup>13</sup>C NMR spectra (see Fig. 1c and d, respectively for the DBUOH results; see the ESI<sup>†</sup> for the data for the other compounds). The peaks in all NMR spectra were assigned using the HMQC spectra (see ESI<sup>†</sup>). The FT-IR spectra of the alkylcarbonate salts contain peaks due to the out-of-plane vibration of the carbonate group near  $835 \text{ cm}^{-1}$  (see Fig. 88†).

The thermogravimetric analysis (TGA) curves for the carbonate salts of the HAMs indicate that decarbonation of HAM-CO<sub>2</sub> commences in the range 55-65 °C and ends near 90-100 °C (Fig. 2). However, the TGA weight loss occurring below 120 °C appeared larger than the percentages of CO<sub>2</sub> per amidine moiety in the expected 1:1 alkylcarbonate salts of DBUOH, (DBUOH)<sub>2</sub>, and (DBNOH)<sub>2</sub>. It is most likely that the excess weight loss occurred due to the moisture adsorbed onto hygroscopic salts while the HAM-CO<sub>2</sub> salts were loaded into TGA sample pans. To exclude moisture from TGA weight loss data, the carbonated salt of DBUOH was prepared in situ by flowing anhydrous CO2 gas into the TGA chamber loaded with a DBUOH sample pan at room temperature. The TGA curve for the resultant salts showed weight loss corresponding to the percentage of CO2 in an DBUOH-CO2 adduct (see Fig. S9<sup>†</sup>). This result indicates that the HAM

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Fig. 1 Reversible  $CO_2$  capture by HAMs. (a) The chemical structures of the HAMs investigated in this study, (b) the carbonation and decarbonation reactions of the HAMs, (c) and (d) <sup>1</sup>H and <sup>13</sup>C NMR spectra of DBUOH and DBUOH-CO<sub>2</sub>, respectively (see Fig. S5 for peak assignment<sup>†</sup>).

compounds comprised of equal numbers of amidine and hydroxyl groups form a 1:1 complex with  $CO_2$  in the absence of water. Theoretical capture capacities of DBUOH, (DBUOH)<sub>2</sub>, and (DBNOH)<sub>2</sub> are 224, 225, and 263 mg  $CO_2/g$  HAM, respectively.

To confirm that alkylcarbonate salts, not bicarbonate salts, form upon bubbling  $CO_2$  into the HAM solutions, we obtained two types of salts by bubbling  $CO_2$  into two different solutions of DBUOH in THF without and with one equivalent of water, respectively, and compared their <sup>1</sup>H and <sup>13</sup>C NMR spectra (Fig. S10†). The salts obtained from the anhydrous DBUOH solution exhibited different peak positions and splitting patterns in <sup>1</sup>H NMR spectra when compared with those obtained from the solution of a 1:1 DBUOH/water mixture. This result indicates that the salts formed by bubbling  $CO_2$  into anhydrous HAM solutions are exclusively alkylcarbonate forms.

Although the HAMs can form bimolecular complexes with  $CO_2$  in a quantitative manner in their solution or liquid states, their complexation reactions are sluggish when they are solid.



Fig. 2 TGA curves for the three carbonated salts of the HAMs generated by bubbling  $CO_2$  gas into their liquid or solution states.



**Fig. 3** TGA curves showing the  $CO_2$  uptake by neat HAMs and HAM/silica mixtures under a  $CO_2$  flow of 100 mL min<sup>-1</sup> at 25 °C. (a) Neat HAM samples (2 mg each), (b) HAM/silica mixtures with a HAM content of 35%.

Fig. 3 shows the TGA curves that describe the progress of the complexation reactions between neat HAM samples and CO<sub>2</sub>; liquid DBUOH absorbed nearly an equimolar amount of CO<sub>2</sub>, whereas, solid (DBUOH)<sub>2</sub> and (DBNOH)<sub>2</sub> absorbed only approximately 0.1 equivalent of CO<sub>2</sub> during the same duration of exposure to a CO<sub>2</sub> atmosphere. The sluggish solid state reactions are most likely due to the slow diffusion of CO<sub>2</sub> gas through solid absorbents.

To facilitate the carbonation process without dissolving the HAMs in a solvent, the solid HAMs must have sufficiently large surface area. Hence, the HAM compounds were impregnated into porous supports consisting of silica gel particles. Solutions of the HAMs in anhydrous THF were mixed with pre-baked, dry amorphous silica gel particles, and subsequent solvent evaporation under reduced pressure resulted in silica-supported HAMs (HAM/silica) as powders. The liquid DBUOH also becomes a powdery solid on mixing with silica for contents less than 40%. To test their capture capacity, the HAM/silica were baked at 110 °C in a TGA sample pan under a nitrogen stream and then exposed to a CO<sub>2</sub> stream. Fig. 3b shows that the HAMs impregnated into silica with a content<sup>15</sup> of 35% exhibit faster CO<sub>2</sub> absorption with higher efficiencies than the neat samples, the results for which are shown in Fig. 3a. The silica-impregnated (DBUOH)<sub>2</sub> and (DBNOH)<sub>2</sub> absorbed CO<sub>2</sub> of 0.6-0.8 equivalents to the amidine moiety, which are much higher than those with the corresponding neat HAMs. We anticipate that the capture capacity of the HAM/silica mixtures might be further improved by impregnating the HAMs into other types of porous solid supports.

We studied the reversibility of the CO<sub>2</sub> capture and release behaviors of the HAM/silica mixtures. The changes in sample weight were recorded *in situ* on a TGA instrument; the flow gas and temperature were alternated between two conditions, 100 mL min<sup>-1</sup> of N<sub>2</sub> flow at 65 °C and 100 mL min<sup>-1</sup> of CO<sub>2</sub> flow at 25 °C. The resulting TGA curves are shown in Fig. 4: the carbonation and decarbonation of the HAMs impregnated into silica occur reversibly. In all experimental runs, the loss of the HAMs was negligible. Although the HAM/silica mixtures contain approximately 65% inactive silica, the CO<sub>2</sub> sorption capacities with respect to the total sorbent weight are still comparable to those of the other supported amine sorbents reported.<sup>16</sup>

In conclusion, we have synthesized hydroxyalkylamidine derivatives that can capture, store, and release  $CO_2$  gas in clean and dry conditions at low temperatures. These new





**Fig. 4** Reversible CO<sub>2</sub> capture and release by silica-supported HAMs with a HAM content of 35%. (a) DBUOH/silica, (b) (DBNOH)<sub>2</sub>/ silica, where capture was performed at 25 °C with a CO<sub>2</sub> flow rate of 100 mL min<sup>-1</sup> and release at 65 °C with a N<sub>2</sub> flow rate of 100 mL min<sup>-1</sup>. In these graphs, mg CO<sub>2</sub>/g HS and mg CO<sub>2</sub>/g H are the weight of CO<sub>2</sub> (in mg) per gram of the HAM/silica mixture (HS) and HAM (H), respectively.

compounds can be used to store pure  $CO_2$  gas in the solid state at ambient temperature. In particular, their volatile-free  $CO_2$ capture and release conditions might enable their application in the removal of  $CO_2$  impurities from the sources of gaseous fuels or in the reduction of indoor  $CO_2$  concentrations in poorly-ventilated spaces such as found in submarines or aeroplanes. The combination of the HAMs with ionic liquids,<sup>17,18</sup> or the utilization of HAM-CO<sub>2</sub> as a solid  $CO_2$ source in new synthetic chemistry<sup>19</sup> are of interest for future study.

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