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Reversible systems based on CO_2, amino-acids and organic superbases†

Gonçalo V. S. M. Carrera,* Noémi Jordão, Miguel M. Santos, Manuel Nunes da Ponte and Luís C. Branco*

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A group of amino-acids from a chiral pool in combination with two organic superbases (DBU or TMG) and CO_2 was used to prepare carbamate-based ionic liquids and molten salts. The compounds obtained were characterized by ^{1}H NMR, ^{13}C NMR, FTIR, solubility profiles in reference solvents and DSC thermal analysis, including their decomposition temperature evaluation, which permitted us to check the stability/reversibility of the carbamate based salts. It's possible to tune the temperature of CO_2 release according to the superbase tested as cation and the characteristics of the side chains of the amino-acids. Moreover, it was possible to solubilize a considerable variety of these carbamate functionalized amino-acids in conventional solvents.

Introduction

CO_2 capture and reversible release, one of the focuses in the present study, is an important and initial step in the process of recycling and valorization of CO_2. The main objective is to minimize the effects of anthropogenic accumulation of CO_2 in the atmosphere.[1] Traditionally, this waste chemical can be used as C1 synthon to obtain fuels and platform/commodity chemicals such as CO, formic acid, methanol, methane, common carboxylic acids, esters, lactones, carbonates, polycarbonates, carbamates, ureas, among others. Photochemical technologies that mimic photosynthesis,[2,3] photoelectrochemical and electrochemical systems,[3] the use of metal catalysts,[4] organic chemistry methodologies,[5] enzymatic[6] and biological transformations[7] are relevant strategies that are being used for CO_2 valorisation. One of the most significant obstacles that preclude a massive application of CO_2 as C1 synthon is its poor reactivity and associated economic viability.

In a different context, Jessop *et al.*[8] reported the reversible formation of ionic liquids, by reacting CO_2 with an alcohol as nucleophile, in the presence of an organic superbase, to obtain a liquid carbonate. The reaction is straightforward and could be reverted and CO_2 released by heating and/or by introduction of an inert gas. Afterwards other aspects of this paradigm were studied and explored such as, the use of other gases (SO_2, COS and CS_2) as elements of reversibility,[9] test of different nucleophiles such as amines,[10,11] amino-alcohols[12] and amino-esters,[13] study of the differences between different types of organic superbases and presence of multiple nucleophilic functionalities in the same molecule.[10] Moreover, recent applications of this concept as systems with switchable polarity and volatility in reactions and/or extractions were also developed.[14]

Simultaneously, studies in the field of CO_2 capture were developed that have the potential to compete with the widespread method applied in industry for more than 60 years, the method is based on aqueous solutions of alkanolamines and the main drawbacks consist in solvent loss, degradation and high energy demand.[15] In order to circumvent such constraints, task-specific ionic liquids were studied.[16–21] The combination of negligible volatility associated with the presence of specific functionalities highlight the potential of application of such class of compounds. The high price in combination with the number of synthetic steps required to prepare these compounds are major obstacles in order to produce at large scale.

The present work consists in the preparation of reversible ionic liquids in one single step with maximized yields in the presence of CO_2 (as element of reversibility), low-cost organic superbases and amino-acids from chiral pool (as nucleophiles). Relevant physico-chemical properties of novel amino-acid carbamate based salts have been evaluated. Such type of system may constitute an effective and cheap tool for CO_2 capture and release, *in situ* manipulation of enantiomeric-dependent characteristics of chemical systems in particular for application as basic catalysis in Knoevenagel condensation, Henry, Direct Aldol and Mannich reactions (as some examples). Manipulation of ionic conductivity, reversible manipulation of solubilities of natural compounds and protection of amine group of aminoacids are other potential applications of the systems here reported.

Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, CQFB/REQUIMTE, 2829-516 Caparica, Portugal. E-mail: gvc11717@fct.unl.pt; l.branco@fct.unl.pt

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Results and discussion

Using a set of amino-acids from chiral pool (AA: glycine, L-alanine, L-valine, L-leucine, L-phenylalanine, D,L-tryptophan – organized by increasing substituent size) and two selected organic superbases (SB: DBU and TMG), a series of carbamate based salts were prepared using CO_2 as functionalization element as indicated in Fig. 1.

Two equivalents of superbase *per* amino-acid unit were added to assure that both acidic functionalities (carboxylic acid and carbamic acid) in amino-acid derived moiety are deprotonated (di-anion). Release of CO_2 from the prepared salts can be performed after heating the samples. This synthetic methodology start from naturally and commercially available chemicals allowing the preparation of reversible chiral ionic liquids and molten salts in a single step.

A detailed spectral analysis was carried out in order to follow the reactions, as well as to characterize the final compounds.

Regarding specifically to the TMG based compounds (Table 1) it is possible to check, based on FTIR spectra, that TMG is fully protonated in all tested cases.

As argument, neutral TMG has one intense band at 1592 cm^{-1},[22] characteristic of symmetrical C=N stretching in guanidine core,[23] while protonated TMG has two characteristic bands in the region between 1650 and 1610 cm^{-1}. The higher frequency band (corresponding to out of phase deformation planar mode of NH_2 from guanidine core[23]) is detected exclusively when TMG is protonated (cation) as observed for prepared compounds. ^{13}C and ^{1}H-NMR confirm this hypothesis in particular the neutral TMG possess peaks at 166.20 (^{13}C-NMR) and 2.61 ppm (^{1}H-NMR), corresponding to the chemical shifts of quaternary carbon of guanidine core and protons from methyl group, respectively, obtained in deuterated DMSO. Differently the NMR spectra of prepared salts presents characteristic peaks at ~163 ppm in ^{13}C-NMR spectra and chemical shifts >2.75 ppm in ^{1}H-NMR for equivalent nucleus which can indicate the presence of $TMGH^+$. Concerning the anion based on amino-acids from the chiral pool, two possibilities arise, one corresponds to the product of deprotonation of the amine group of the amino-acid while another hypothesis corresponds to the product of deprotonation of the amine group and reaction with CO_2 to obtain the carbamate based salt. According simulations performed, if the first hypothesis corresponds to the real identity of the anionic moiety of each salt the ^{1}H-NMR chemical shift of the proton(s) associated to carbon alpha of the amino-acid would be significantly more shielded than the equivalent proton(s) in the hypothesis of carbamate formation or zwitterionic amino-acid. The spectra of the products show in all cases that the proton(s) in carbon alpha are significantly more deshielded than in parent zwitterionic amino-acids, a clear indication of functionalization with CO_2 to attain carbamates. Moreover, in the ^{13}C-NMR spectra, each compound presents more than one peak in the region between 172 to 176 ppm corresponding to quaternary carbons of carboxylate and carbamate functionality. In most of the situations more than two peaks arise in that spectral region, indication that probably there are sterical constraints and no free rotation of all bonds around carboxylate and carbamate functionalities should be also considered. The localization of the carbamate functionality was based on spectral comparison (^{13}C-NMR) before and after reaction with CO_2 in the spectra of isoleucine based amino-ester reported by Yamada's group.[13] Additionally, FTIR spectra of these TMG based compounds (ESI Table S1†) show characteristic bands associated to carbamate functionality that were unveiled using different methods (direct comparison with values present in the literature for the same functionality[13,17] as well as contrast between the FTIR spectra of ammonium carbamate and ammonium chloride[22] in combination with previous work[24]).

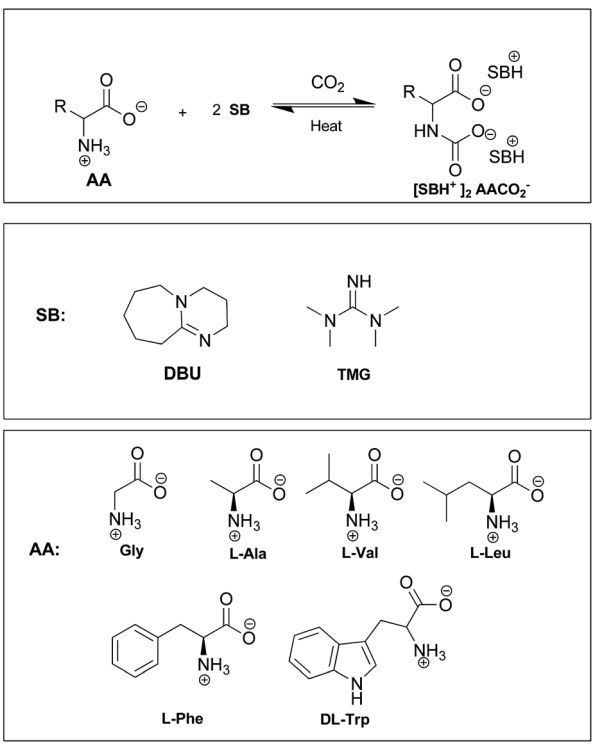

Fig. 1 Preparation of carbamate based reversible ionic liquids using six amino-acids from the chiral pool and two organic superbases.

Similarly to TMG based salts, DBU based salts were characterized by ^{1}H-NMR, ^{13}C-NMR and FTIR (Table 2) in order to check the identity of the products and also to evaluate the efficiency of this synthetic method for other organic superbases. Based on FTIR analysis/contrast between DBU and the products of reaction, were the former presents two C=N vibration bands (one intense at 1618 cm^{-1} and a less intense in the region ~1650 cm^{-1} (ref. 22 and 25)), and the prepared salts in this work present an intense band in the region of 1648–1650 cm^{-1}; is possible to conclude, according the reported observation of Galezowski *et al.*[25] that DBU moiety of the prepared salts is protonated. These results are also confirmed by ^{13}C-NMR according with characteristic DBU quaternary carbon peak at 159.54 ppm in DMSO, comparing with equivalent carbon in DBU moiety of our compounds (~164 ppm in DMSO) as a clear indication that DBU is protonated in all prepared salts.

Table 1 Characterization of TMG based carbamate salts by ^{1}H-NMR, ^{13}C-NMR and FTIR

Compounds ($TMGH^+$ based carbamates)	FTIR cm^{-1} $TMGH^+$(1), $TMGH^+$(2), (TMG)	^{13}C-NMR ppm $TMGH^+$ $C(N_2)NH_2^+$, (TMG) $C(N_2)NH$	^{13}C-NMR ppm COO^- and $NCOO^-$	^{1}H-NMR ppm $TMGH^+$ $CN(CH_3)_2$, (TMG) $CN(CH_3)_2$	^{1}H-NMR ppm aminoacid derived carbamate $CHR(NCOO^-)COO^-$ (aminoacid), $(CHR(NH_3^+)COO^-)$
$[TMGH^+]_2$ $[GlyCO_2^-]$	1647.53 s, 1608.45 s (1592 s)	162.91 (166.20)	172.380, 172.385	2.78 (2.61)	3.18 (2.92)
$[TMGH^+]_2$ $[AlaCOO^-]$	1648.1 s, 1612.1 s (1592 s)	163.47 (166.20)	174.79, 174.81	2.75 (2.61)	3.34 (3.14)
$[TMGH^+]_2$ $[ValCOO^-]$	1648.29 s, 1613.37 s (1592 s)	162.88 (166.20)	174.18, 174.20	2.81 (2.61)	3.23 (2.98)
$[TMGH^+]_2$ $[LeuCOO^-]$	1647.60 s, 1607.97 s (1592 s)	163.25 (166.20)	175.54, 175.56, 175.57, 175.59	2.78 (2.61)	3.35 (3.08)
$[TMGH^+]_2$ $[PheCOO^-]$	1649.3 s, 1612.0 s (1592 s)	162.77 (166.20)	174.25, 174.26, 174.30, 174.33, 174.34	2.80 (2.61)	3.61 (3.17–3.51)
$[TMGH^+]_2$ $[TrpCOO^-]$	1648.1 s, 1612 s (1592 s)	162.72, 162.66 (166.20)	175.43, 175.44, 175.46, 175.48, 175.67	2.81 (2.61)	3.61 (3.55)

Concerning the amino-acid based component, in order to verify if the carbamate functionality was obtained, a similar approach respective to TMG based salts was followed.

Similarly in ^{1}H-NMR spectra the proton(s) in carbon alpha of the amino-acid moiety are more deshielded in the prepared salts than in the original zwitterionic amino-acids, indicative of carbamate formation, already justified for TMG based salts.

The ^{13}C-NMR characteristic peaks in the region of ~175 ppm are indicative of coexistence of carboxylate and carbamate functionalities in the same salt, and the FTIR bands are also indicative of carbamate functionality (ESI Table S2†).

Table 3 summarizes some physico-chemical properties such as glass transition temperature (T_g), melting point (mp), decomposition temperature (T_d) and solubilities in conventional solvents (water, acetonitrile, DMSO, dichloromethane and acetone). Differently from the work of Fukumoto *et al.*,[26] that prepare different ionic liquids ([EMIM] as cation and different amino-acids as anions), and obtained exclusively glass forming liquids; in our case, with the use of a superbase and CO_2 as element of functionalization of the amino-acids, it is possible to obtain different ionic materials such as crystalline solids, semi-crystalline materials and liquids at room temperature with glass transition temperature according the existence of mp and/or T_g. L-Valine based salts are crystalline solids with mp's of 81.58 and 89.37 °C for the TMG and DBU based compounds respectively, the small difference between mp's is an indication of the low sensitivity of this property respective to the superbases tested, nevertheless, the higher value of mp obtained for $[DBUH]_2$[ValCOO] is indicative that probably van der Walls interactions between DBU and carbamate-functionalized Valine is stronger than in equivalent TMG based compound. Other possible explanation is that the positive charge in DBU based cation is less delocalized than in TMG salt. $[DBUH]_2$[AlaCOO] and $[DBUH]_2$[LeuCOO] (considered semi-crystalline materials) are other examples of salts with well-defined melting point. In this case, including this two examples, is possible to consider that the value of mp is even more insensitive to the amino-acid used with the mp following the order Ala > Val > Leu (all with DBU based cation).

To explain such behaviour, probably, entropic factors related with geometry and specifically the increasing number of conformational degrees of freedom from L-alanine to L-leucine can be more relevant than the effect of increasing van der Walls interactions with the increment of the size of alkyl group in the amino-acid. A similar trend is observed for the melting point of methane, ethane and propane, for example.

Considering and comparing the glass-forming liquids and including the semi-crystalline materials (Table 3), the T_g for the DBU based salts present a "U" shaped profile as function of the alkyl chain size with the amino-acid based carbamate salts following the order Gly > Ala < Leu. In this case from Gly to Ala the entropic geometrical factors (as stated for mp) surpass the increment of van der Walls interactions; the reverse occurs from Ala to Leu based carbamate salts. This "U" shape behaviour as function of the size of alkyl chain was observed experimentally for 1-alkyl-3-methylimidazolium salts.[30] Moreover, with the presence and increment of π-bonds in the substituent group of

Table 2 FTIR Selected bands and ^{1}H-NMR, ^{13}C-NMR peaks of DBU based carbamate salts

Compounds ($DBUH^+$ based carbamates)	FTIR cm^{-1} $DBUH^+$ (DBU)	^{13}C-NMR ppm $DBUH^+$ *C*(N)(NH)C, (DBU) *C*(N)$_2$C	^{13}C-NMR ppm COO^- and $NCOO^-$	^{1}H-NMR ppm aminoacid derived carbamate C*H*R($NCOO^-$)COO^- (aminoacid), C*H*R(NH_3^+)COO^-
[$DBUH^+$]$_2$ [$GlyCOO^-$]	1648.96 s (1618)	164.52 (159.54)	173.10, 173.36	3.20 (2.92)
[$DBUH^+$]$_2$ [$AlaCOO^-$]	1649.76 s (1618)	164.32 (159.54)	176.05, 176.08	3.3–3.5 (Superimposed) (3.14)
[$DBUH^+$]$_2$ [$ValCOO^-$]	1649.17 s (1618)	164.29 (159.54)	175.20, 175.21, 175.22, 175.23, 175.28, 175.30, 175.30, 175.33	3.28 (2.98)
[$DBUH^+$]$_2$ [$LeuCOO^-$]	1648.3 s (1618)	164.10 (159.54)	176.54, 176.58	3.38–3.46 (3.08)
[$DBUH^+$]$_2$ [$PheCOO^-$]	1648.3 s (1618)	164.32 (159.54)	174.76, 174.77, 174.78, 174.79, 174.81, 174.83, 174.84, 174.85	3.68 (3.17–3.51)
[$DBUH^+$]$_2$ [$TrpCOO^-$]	1649.8 s (1618)	164.33 (159.54)	175.64 (large and assymetric)	3.77 (3.55)

the amino-acid (Phe to Trp based carbamate salts) an increment of the value of T_g is observed. In this case, the increasing π–π interactions are responsible for such behaviour. Considering the TMG based salts that present a T_g, a similar trend, as observed for DBU based salts. Considering the effect of the selected organic superbase as cation, TMG leads to salts with higher T_g value than with DBU (for Leu, Phe, Trp). In this case, contrarily to the observed melting points for the L-valine carbamate based salts, geometrical factors (TMG more rigid), an extended π system in TMG based cation as well as the possibility of strong interaction by six ring hydrogen-bond with carboxylate and carbamate moieties (Fig. 2) might be more important than the increased van der Walls interactions and reduced capacity of delocalization of the positive charge in DBUH.

An important parameter to consider in order to assess the stability/reversibility of these carbamate based salts is the decomposition temperature (T_d) associated to CO_2 loss. In this case, considering the results presented in Table 3, TMG based salts, in most of the cases, showed higher T_d than DBU based salts (in the other cases, and according to the experimental results, there is uncertainty in establishing a comparative analysis).

Probably the reason for the higher values obtained with TMG is based on the stabilization of the carbamate functionality by a six ring hydrogen-bond interaction with $TMGH^+$ (Fig. 2), similarly to the previously reported by Heldebrandt *et al.*[31] for the carbonate functionality. Moreover, Jackson *et al.*[32] highlight the importance of the hydrogen bond interaction in stabilization of the carbamate functionality, based on computational chemistry methodologies. They suggested a specific stabilization by hydrogen bond interaction leads to reduction of N–COO^- bond by conjugation as illustrated in Fig. 2.

There is an inverse correlation between T_d and the size of the amino-acid (R-) substituent in DBU based salts (Table 3) with the order Gly > Ala > Val > Leu > Phe > Trp being followed. In the computational study of Jackson *et al.*,[32] some of the more hindered amines and amino-alcohols lead to less favourable

Table 3 Thermal characterization and solubilities in reference solvents of the prepared salts[a]

				Solubilities g/1000 g r.t.				
Compound	Physical State	mp (T_g) (°C)	T_d (°C)	Water (parent amino-acid*)	ACN	DMSO	DCM	Acetone
[$TMGH^+$]$_2$ [$GlyCOO^-$]	White solid	—	>120	264 (184)** (ref. 27)	<9	70	<4	<5
[$DBUH^+$]$_2$ [$GlyCOO^-$]	White paste	(−22.26)	106.36	478 (184)** (ref. 27)	<3	34	<2	<4
[$TMGH^+$]$_2$ [$AlaCOO^-$]	White paste	—	>88	157 (167)*** (ref. 28)	<4	260	<4	<4
[$DBUH^+$]$_2$ [$AlaCOO^-$]	White solid	92.11 (−48.46)	101.77	253 (167)*** (ref. 28)	273	155	154	<15
[$TMGH^+$]$_2$ [$ValCOO^-$]	White solid	81.58	>120	213 (85)** (ref. 28)	<8	319	<2	<10
[$DBUH^+$]$_2$ [$ValCOO^-$]	White paste	89.37	96.35	158 (85)** (ref. 28)	66	172	<4	<19
[$TMGH^+$]$_2$ [$LeuCOO^-$]	Transparent gel	(−27.86)	109.07	138 (23)** (ref. 27)	<5	97	<3	<6
[$DBUH^+$]$_2$ [$LeuCOO^-$]	Yellow paste	87.05 (−41.46)	95.6	204 (23)** (ref. 27)	<7	161	<3	<5
[$TMGH^+$]$_2$ [$PheCOO^-$]	White paste	(−15.70)	93.79	258 (26)** (ref. 29)	398	181	265	23
[$DBUH^+$]$_2$ [$PheCOO^-$]	Yellow gel	(29.22)	86.91	228 (26)** (ref. 29)	357	227	188	23
[$TMGH^+$]$_2$ [$TrpCOO^-$]	Orange paste	(−3.84)	>74	16 (10)** (ref. 28)	<6	217	<3	<12
[$DBUH^+$]$_2$ [$TrpCOO^-$]	Orange gel	(−8.21)	79.62	120 (10)** (ref. 28)	<3	114	140	<3

[a] mp: melting point, T_g: glass transition temperature, T_d: decomposition temperature, ACN: acetonitrile, DMSO: dimethylsulfoxide, DCM: dichloromethane. * When required the solubilities of the parent amino-acids in water were converted from g/1000 g of water to g/1000 g of solution. ** Measured at 20 °C, *** Measured at 25 °C. In ref. 28 the solubilities are presented in g L^{-1}.

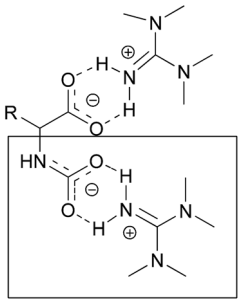

Fig. 2 Effect of stabilization of the carbamate functionality based on six-ring hydrogen bond interaction with $TMGH^+$.

equilibrium for the reaction of CO_2 capture. A similar trend was observed for the TMG based salts (with uncertainties associated to some of the studied salts – which precludes a complete definition of order). According to this analysis, the combined use of TMG and amino-acids with small substituent (R-) groups lead to the more stable carbamates. On the contrary the use of DBU and amino-acids with large substituent groups lead to more reversible CO_2 capture systems. According to the obtained results rationalized in this discussion, it is possible to associate the wide range of values of T_d, with the possibility of tuning the temperature of CO_2 release according the judicious choice of an amino-acid and organic superbase. In this context such described systems can be potentially used for capture and release of CO_2.

Another relevant issue is addressed to the generally poor solubility of amino-acids in organic solvents, fact that creates difficulties when processing such compounds, (*e.g.* peptide synthesis). Herein, we also tested the solubility of amine-protected amino-acids in different conventional solvents. All the prepared compounds are soluble in water and DMSO. $[DBUH]_2[AlaCOO]$ is also soluble in acetonitrile and dichloromethane while $[DBUH]_2[ValCOO]$ and $[DBUH]_2[TrpCOO]$ are only soluble in acetonitrile and dichloromethane respectively. $[TMGH]_2[PheCOO]$ and $[DBUH]_2[PheCOO^-]$ are examples of salts completely soluble for all tested organic solvents.

The possibility to solubilize a variety of amino-acids (especially based on DBU) in conventional volatile organic solvents opens perspectives on the processing of amino-acids. Moreover such systems have the potential to constitute effective basic catalysts in reference reactions and open the possibility of tunning of ionic conductivity using CO_2 and increment of temperature as triggers. Finally, reversible manipulation of solubilities of natural compounds and protection of amine group of aminoacids are other potential applications of the systems here reported.

Experimental

Materials and methods

Glycine from BDH with 99% purity, L-alanine with a purity of 99%, L-valine with a purity of 99% and L-leucine (99% purity) were supplied by Alfa Aesar. L-Phenylalanine and D,L-tryptophan with purity higher than 99% were supplied by Merck. 1,1,3,3 Tetramethylguanidine (TMG), 99%, was supplied by Sigma-Aldrich (water removed using molecular sieves), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), with purity of at least 99%, was provided by Fluka (with water removed using molecular sieves) and dichloromethane, p.a. grade, supplied by Sigma-Aldrich. 99 998 mol% carbon dioxide was supplied by air liquid.

General synthetic procedures

The synthesis were performed in a cylindrical high pressure steel reactor (11 mL) with sapphire windows at both ends.

In a general reaction, 2 equivalents of superbase dissolved in dichloromethane were added to 1 equivalent of amino-acid suspended in the same solvent. To the resultant reaction mixture CO_2 was introduced until a pressure of 20 bar was reached. The reactions were performed at room temperature and the mixture between elements of reaction was promoted using magnetic stirrer during the reactional period. After that period the solvent was removed by *in situ* continuous stream of CO_2 during 2 hours at room temperature. The resultant product was stored at a temperature of approximately 7 °C.

The prepared compounds were characterized ^1H and ^{13}C NMR recorded on a Bruker AMX400 spectrometer. Chemical shifts are reported downfield in parts per million from a tetramethylsilane reference. IR spectra were recorded on a Perkin Elmer FTIR Spectrometer, Spectrum 1000 and Spectrometer FTIR Bruker Tensor 27. The samples were prepared in a KBr matrix. DSC analysis was carried out by using a TA Instruments Q-series TM Q2000 DSC with a refrigerated cooling system. The sample is continuously purged with 50 mL min^{-1} nitrogen gas and 2–8 mg of salt was crimped into an aluminum standard sample pan with lid. The samples were submitted an isothermal step (40 °C, 10 minutes), cooled to −90 °C (20 °C min^{-1}) and then heated to 120 °C (20 °C min^{-1}). The glass transition temperature, the melting point and the decomposition temperature were determined in the heating process. The decomposition temperature was determined using the inflection point of the endothermic behavior. The solubility in reference solvents was attained using the following method: to a weighted sample of a carbamate salt prepared was added solvent, drop by drop, until an homogeneous solution arises after homogenization using a vortex. Such mixture was weighted and the minimum quantity of solvent required to solubilize each product was assessed.

1. Bis(1,1′,3,3′-tetramethylguanidinium) 2-(carboxylatoamino) acetate. $[TMGH]_2$ [GlyCOO]. It was prepared following the synthetic procedure to obtain aminoacid based carbamate salts: 0.3 g (2 eq.) of tetramethylguanidine dissolved in dichloromethane was added to 0.097 g. (1 eq.) of glycine suspended in the same solvent (total volume of solvent 3 mL). The reaction mixture was stirred at room temperature in a atmosphere of 20 bar of CO_2 during 9–30 h. The product is a white solid obtained in 62% yield. ^1H-NMR (400 MHz, d_6-DMSO): δ: 2.78 (s, 24H), 3.18 (s, 2H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 39.23, 46.21, 162.91, 172.38, 172.39. FTIR (KBr): 3307, 3281, 3106, 3009, 2997, 2954, 2916, 2851, 2808, 2719, 1700, 1647, 1608, 1561, 1561, 1489, 1474, 1446, 1433, 1412, 1373, 1317, 1258,

1197, 1145, 1117, 1084, 1078, 1063, 1038, 1008, 979, 931, 892, 872, 831, 810, 727, 703, 682, 668 cm^{-1}.

2. Bis(2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepin-1-ium) 2-(carboxylatoamino)acetate. [DBUH]$_2$ [GlyCOO]. Using 0.3 g. (2 eq.) of DBU and 0.073 g. (1 eq.) of glycine and 3 mL. of dichloromethane the reaction proceed at room temperature during 7–10h under an atmosphere of 20 bar of CO_2. The product is a white paste obtained in a 52% yield. ^{1}H-NMR (400 MHz, d_6-DMSO): δ: 1.58-1.64 (m, 12H), 1.85 (quint, $J = 4$ Hz, 4H), 2.68 (m, 4H), 3.20–3.22 (m, 6H), 3.40 (m, 4H), 3.46–3.48 (m, 4H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 19.50, 23.91, 26.41, 28.45, 31.61, 38.24, 46.34, 47.73, 52.87, 164.52, 173.10, 173.36 ppm. FTIR (KBr): 3423, 3241, 3115, 2937, 2863, 1687, 1648, 1603, 1593, 1501, 1472, 1437, 1403, 1372, 1324, 1301, 1270, 1245, 1207, 1160, 1107, 1044, 1008, 984, 930, 892, 831, 704, 687, 664, 633, 609 cm^{-1}.

3. Bis(1,1′,3,3′-tetramethylguanidinium) (L)-2-(carboxylatoamino)propanoate [TMGH]$_2$ [AlaCOO]. Using 0.3 g. (2 eq.) of tetramethylguanidine, 0.1162 g. (1 eq.) of L-alanine, 3 mL. of dichloromethane and 20 bar of CO_2, the reaction proceed during 6–50h at room temperature. The product was obtained as a white paste with an isolated yield of 37%. ^{1}H-NMR (400 MHz, d_6-DMSO): δ: 1.10 (d, $J = 8$ Hz, 2H), 2.75 (s, 24H), 3.34 (ls, 1H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 19.25, 39.21, 51.66, 163.70, 174.79, 174.81 ppm. FTIR (KBr): 3433, 3192, 2973, 2941, 2819, 1668, 1654, 1648, 1612, 1566, 1561, 1556, 1546, 1534, 1528, 1522, 1517, 1508, 1498, 1473, 1465, 1458, 1435, 1411, 1369, 1320, 1302, 1198, 1143, 1091, 1065, 1039, 1009, 989, 875, 830, 703, 669, 662 cm^{-1}.

4. Bis(2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepin-1-ium) (l)-2-(carboxylatoamino)propanoate [DBUH]$_2$ [AlaCOO]. It was used 0.3 g. of DBU (2 eq.), 0.0874 g. (1 eq.) of L-alanine, 3 mL. of dichloromethane and 20 bar of CO_2. The reaction mixture was stirred during 8–45 h at room temperature. The product was obtained as a white solid in a 62% yield. ^{1}H-NMR (400 MHz, d_6-DMSO): δ: 1.11 (d, $J = 4$ Hz, 3H), 1.58–1.65 (m, 12H), 1.84 (quint, $J = 6$ Hz, 4H), 2.65–2.68 (m, 4H), 3.21 (t, $J = 4$ Hz, 4H), 3.38–3.46 (m, 9H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 19.63, 20.26, 24.00, 26.49, 28.49, 31.86, 38.89, 47.74, 51.60, 52.85, 164.32, 176.05, 176.08 ppm. FTIR (KBr): 3409, 3238, 3115, 2971, 2938, 2884, 1691, 1649, 1641, 1589, 1566, 1519, 1412, 1365, 1326, 1309, 1273, 1245, 1209, 1162, 1110, 1094, 1078, 1012, 998, 986, 920, 890, 851, 833, 774, 706, 666, 620 cm^{-1}.

5. Bis(1,1′,3,3′-tetramethylguanidinium) (L)-2-(carboxylatoamino)-3-methylbutanoate [TMGH]$_2$ [ValCOO]. The mixture was stirred during 8 h at room temperature using 0.3 g. of tetramethylguanidine (2 eq.), 0.15270 g. (1 eq.) of L-valine and 3 mL. of dichloromethane as solvent under 20 bar of CO_2. The product was obtained as a white solid in 58% yield. ^{1}H-NMR (400 MHz, d_6-DMSO): δ: 0.78 (d, $J = 8$ Hz, 3H), 0.81 (d, $J = 8$ Hz, 3H), 2.00 (hep, $J = 8$ Hz, 1H), 2.81 (s, 24H), 3.23 (ls, 1H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 18.54, 19.76, 30.67, 39.24, 62.17, 162.88, 174.18, 174.20 ppm. FTIR (KBr): 3420, 3213, 2969, 1672, 1648, 1613, 1587, 1567, 1508, 1471, 1456, 1411, 1397, 1372, 1329, 1271, 1191, 1178, 1142, 1091, 1065, 1038, 1008, 980, 949, 924, 901, 875, 830, 775, 752, 715, 703, 664 cm^{-1}.

6. Bis(2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepin-1-ium) (L)-2-(carboxylatoamino)-3-methylbutanoate [DBUH]$_2$ [ValCOO]. DBU (0.3 g., 2 eq.), 0.1146 g. (1 eq.) of L-valine and 3 mL. of dichloromethane were stirred at room temperature during 9 h under 20 bar of CO_2. The product was obtained as a white paste in 72% yield. ^{1}H-NMR (400 MHz, d_6-DMSO): δ: 0.76 (d, $J = 8$ Hz, 3H), 0.80 (d, $J = 8$ Hz, 3H), 1.58–1.64 (m, 12H), 1.84 (t, $J = 6$ Hz, 4H), 2.66 (m, 4H), 3.21 (m, 4H), 3.28 (ls, 1H), 3.39 (m, 4H), 3.45 (m, 4H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 18.35, 19.66, 19.78, 24.02, 26.50, 28.49, 31.03, 31.92, 38.55, 47.74, 52.86, 61.68, 164.29, 175.20, 175.21, 175.22, 175.23, 175.28, 175.30, 175.31, 175.33 ppm. FTIR (KBr): 3407, 3250, 3124, 2937, 2882, 1690, 1649, 1632, 1586, 1583, 1511, 1472, 1438, 1425, 1398, 1371, 1326, 1308, 1271, 1244, 1208, 1162, 1140, 1108, 1092, 1077, 1009, 985, 949, 918, 901, 889, 831, 775, 752, 715, 703, 664, 618 cm^{-1}.

7. Bis(1,1′,3,3′-tetramethylguanidinium) (L)-2-(carboxylatoamino)-4-methylpentanoate [TMGH]$_2$ [LeuCOO]. 0.3 g. (2 eq.) of tetramethylguanidine, 0.1709 g. (1 eq.) of L-Leucine and 3 mL. of dichloromethane were stirred under 20 bar of CO_2 at room temperature during 6 h. The product was obtained as a transparent gel in 42% yield. ^{1}H-NMR (400 MHz, d_6-DMSO): δ: 0.84 (d, $J = 6$ Hz, 3H) 0.86 (d, $J = 6$ Hz, 3H), 1.41 (m, 2H), 2.12 (m, 1H), 2.78 (s, 24H), 3.35 (m, 1H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 22.17, 23.21, 24.40, 42.27, 42.30, 42.31, 42.33, 55.24, 55.26, 163.25, 175.54, 175.56, 175.57, 175.58 ppm. FTIR (KBr): 3281, 3106, 2956, 1688, 1647, 1607, 1566, 1518, 1434, 1410, 1373, 1316, 1297, 1185, 1144, 1118, 1085, 1064, 1038, 1009, 979, 944, 924, 873, 831, 727, 703, 668 cm^{-1}.

8. Bis (2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepin-1-ium) (L)-2-(carboxylatoamino)-4-methylpentanoate [DBUH]$_2$ [LeuCOO]. A mixture of 0.3 g. of DBU (2 eq.), 0.1295 g. of L-Leucine (1 eq.) in 3 mL. of dichloromethane were stirred at room temperature under 20 bar of CO_2 during 8 h. The product was obtained pale yellow paste in 46% yield. ^{1}H-NMR (400 MHz, d_6-DMSO): δ: 0.85 (d, $J = 8$ Hz, 6H), 1.29–1.35 (m, 1H) 1.38–1.45 (m, 1H), 1.60–1.68 (m, 12H), 1.84 (quint, $J = 4$ Hz, 4H), 2.64–2.66 (m, 4H), 3.21 (t, $J = 4$ Hz, 4H), 3.38–3.46 (m, 13H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 19.75, 22.39, 23.30, 24.08, 24.42, 26.56, 28.51, 32.20, 38.71, 43.23, 43.25, 43.27, 43.29, 47.72, 52.80, 54.97, 164.10, 176.54, 176.58 ppm. FTIR (KBr): 3417, 3249, 3198, 3115, 2938, 1692, 1648, 1625, 1614, 1603, 1568, 1563, 1516, 1472, 1438, 1406, 1371, 1325, 1296, 1271, 1243, 1208, 1188, 1161, 1107, 1090, 1079, 1009, 984, 944, 916, 846, 831, 768, 703, 669 cm^{-1}.

9. Bis(1,1′,3,3′-tetramethylguanidinium) (L)-2-(carboxylatoamino)-3-phenylpropanoate [TMGH]$_2$ [PheCOO]. Tetramethylguanidine (0.3 g – 2 eq.) and 0.2133 g (1 eq.) of L-phenylalanine in 3 mL of dichloromethane under 20 bar of CO_2 were stirred at room temperature during 7–10 h. The product was obtained as a white paste with an isolated yield of 49%. ^{1}H-NMR (400 MHz, d_6-DMSO): δ: 2.80 (s, 24H), 2.99 (dd, $J_1 = 12$ Hz, $J_2 = 4$ Hz, 1H), 3.61 (ls, 1H), 7.10–7.27 (m, 5H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 39.25, 57.69, 125.39, 127.61, 129.48, 140.08, 162.77, 174.25, 174.26, 174.30, 174.33, 174.34 ppm. FTIR (KBr): 3397, 3191, 2962, 2817, 2738, 1690, 1649, 1612, 1566, 1560, 1556, 1546, 1535, 1506, 1496, 1471, 1455, 1432, 1410, 1373, 1338, 1318, 1307, 1292, 1259, 1235, 1195, 1164, 1151, 1145, 1092, 1065, 1038, 1009, 976, 912, 849, 831, 781, 746, 702, 680, 660, 603 cm^{-1}.

10. Bis(2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepin-1-ium) (L)-2-(carboxylatoamino)-3-phenylpropanoate [DBUH]$_2$ [PheCOO]. A mixture of 0.3 g. of DBU (2 eq.), 0.16125 g of L-phenylalanine (1 eq.) in 3 mL. of dichloromethane were stirred at room temperature under 20 bar of CO_2 during 7–30 h. The product was obtained as yellow gel in 48% yield. ^{1}H-NMR (400 MHz, d_6-DMSO): δ: 1.57–1.64 (m, 12H), 1.83 (quint, $J = 4$ Hz, 4H), 2.64–2.66 (m, 4H), 2.83 (dd, $J_1 = 14$ Hz, $J_2 = 6$ Hz, 1H), 2.97 (dd, $J_1 = 14$ Hz, $J_2 = 6$ Hz, 1H), 3.19 (t, $J = 4$ Hz, 4H), 3.39 (t, $J = 4$ Hz, 4H), 3.44–3.46 (m, 4H), 3.68 (ls, 1H), 7.09–7.28 (m, 5H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 19.61, 23.98, 26.47, 28.48, 31.87, 38.47, 47.73, 52.86, 57.46, 125.27, 127.48, 129.56, 140.16, 164.32, 174.76, 174.77, 174.78, 174.79, 174.81, 174.83, 174.84, 174.85 ppm. FTIR (KBr): 3415, 3243, 3116, 3032, 2936, 2861, 2808, 1690, 1651, 1648, 1643, 1631, 1619, 1602, 1585, 1578, 1571, 1566, 1560, 1555, 1546, 1535, 1529, 1523, 1518, 1508, 1495, 1472, 1453, 1444, 1437, 1401, 1373, 1322, 1307, 1292, 1270, 1243, 1206, 1158, 1105, 1090, 1075, 1029, 1009, 996, 983, 970, 912, 886, 829, 776, 746, 702, 682, 663, 634, 606 cm^{-1}.

11. Bis(1,1′,3,3′-tetramethylguanidinium) (D,L)-2-(carboxylatoamino)-3-(1*H*-indol-3-yl)propanoate [TMGH]$_2$ [TrpCOO]. Tetramethylguanidine (0.3 g–2 eq.) and 0.2636 g (1 eq.) of D,L-tryptophan in 3 mL. of dichloromethane under 20 bar of CO_2 were stirred at room temperature during 7–30 h. The product was obtained as a orange paste in 44% yield. ^{1}H-NMR (400 MHz, d_6-DMSO): δ: 2.81 (s, 25H), 3.13 (dd, $J_1 = 16$ Hz, $J_2 = 4$ Hz, 1H), 3.61 (ls, 1H), 6.90 (t, $J = 8$ Hz, 1H), 7.00 (t, $J = 6$ Hz), 7.11 (s, 1H), 7.29 (d, $J = 8$ Hz, 1H), 7.50 (d, $J = 8$ Hz, 1H), 10.97 (ls, 1H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 39.22, 56.95, 111.12, 111.89, 117.69, 118.48, 120.37, 123.45, 127.91, 136.09, 162.66, 162.72, 175.43, 175.44, 175.46, 175.48, 175.67 ppm. FTIR (KBr): 3402, 3239, 2962, 2857, 2742, 1663, 1654, 1648, 1636, 1612, 1584, 1577, 1570, 1560, 1545, 1534, 1527, 1521, 1508, 1468, 1456, 1410, 1375, 1357, 1340, 1313, 1292, 1261, 1248, 1230, 1167, 1140, 1096, 1064, 1037, 1007, 985, 862, 829, 746, 737, 704, 660, 623 cm^{-1}.

12. Bis(2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepin-1-ium) (D,L)-2-(carboxylatoamino)-3-(1*H*-indol-3-yl)propanoate. [DBUH]$_2$ [TrpCOO]. Using 0.3 g (2 eq.) of DBU and 0.1993 g (1 eq.) of (D,L)-tryptophan and 3 mL. of dichloromethane the reaction proceed at room temperature during 7–30 h under an atmosphere of 20 bar of CO_2. The product is a orange gel obtained with an isolated yield of 60%. ^{1}H-NMR (400 MHz, d_6-DMSO): δ: 1.55–1.62 (m, 12H), 1.81 (quint, $J = 4$ Hz, 4H), 2.62 (m, 4H), 2.93 (dd, $J_1 = 14$ Hz, $J_2 = 6$ Hz, 1H) 3.11 (dd, $J_1 = 16$ Hz, $J_2 = 4$ Hz, 1H), 3.16 (t, $J = 4$ Hz, 4H), 3.36 (t, $J = 6$ Hz, 4H), 3.42–3.44 (m, 4H), 3.77 (ls, 1H) ppm. ^{13}C-NMR (100 MHz, d_6-DMSO): δ: 19.56, 23.93, 26.45, 28.48, 31.85, 38.42, 47.71, 52.87, 56.89, 110.98, 111.93, 117.70, 118.62, 120.26, 123.34, 128.12, 135.96, 164.33, 175.64 ppm. FTIR (KBr): 3432, 3241, 3119, 3042, 2977, 2933, 2860, 2807, 1692, 1649, 1630, 1620, 1585, 1572, 1556, 1536, 1506, 1469, 1441, 1401, 1370, 1356, 1340, 1324, 1295, 1271, 1245, 1229, 1206, 1160, 1107, 1091, 1075, 1008, 996, 982, 968, 915, 887, 863, 830, 808, 747, 703, 691, 662, 632 cm^{-1}.

Conclusions

A set of reversible carbamate based IL's was prepared using amino-acids from chiral pool, organic superbases and CO_2. The identity of the product was checked by ^{1}H-NMR, ^{13}C-NMR and FTIR. DSC thermal analysis and test of solubilities in reference solvents was performed. Different types of materials were obtained according the existence of T_g and/or mp. These properties and T_d as well, presented regular variation pattern according the side chain of the amino-acid and superbase tested. Based on the values of T_d (CO_2 loss) is possible to obtain more stable carbamates if TMG and amino-acids with small substituent groups are used. In opposite direction the use of DBU and amino-acids with large substituent group lead to more reversible systems. The wide range of temperatures obtained for T_d opens possibility for CO_2 capture system *a la carte* according the amino-acid and superbase used. The possibility of solubilize a great variety of the prepared compounds opens the perspective of processing amino-acids in reference volatile organic solvents.

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