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Exploring reversible reactions between CO_2 and amines

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Abstract—The 'old' chemistry between CO_2 and primary alkylamines has been revisited. Amines **1** and **2**, with appended aromatic fluorophores, reversibly reacted with CO_2 in polar aprotic solvent (e.g. DMSO, DMF) with the formation of carbamic acids **3** and **4**. As a result, strong fluorescence occurred, thus directly reporting on the CO_2 entrapment. Carbamic acids were studied by ^1H and ^{13}C NMR spectroscopy in DMSO-d_6. The carbamate bond, despite being covalent, is reversible and can be broken upon heating or simply flashing solutions with inert gases. Synthesis and evaluation of a CO_2-sensing amino acid-α-naphthylglycine **7** is also reported for potential CO_2 monitoring under biorelevant conditions in aqueous solutions.

1. Introduction

Carbon dioxide (CO_2) is the major greenhouse gas.[1] It constantly circulates in the environment through a variety of processes known as the carbon cycle. Both volcanic eruptions and the decay of plants and animals release CO_2 into the atmosphere.

Oceans, lakes, and rivers absorb CO_2 from the atmosphere. Through photosynthesis, plants collect CO_2 and use it to make their own food, in the process incorporating carbon into new plant tissues and releasing oxygen to the environment as a byproduct. Upon burning of fossil fuels, oil, coal, and natural gas, and wood, huge amounts of CO_2 are released into the air. As a result of these activities, CO_2 in the atmosphere is accumulating faster than the Earth's natural processes can absorb this gas. The CO_2 levels in the atmosphere have risen by 31% over the last 250 years and these concentrations may double or even triple in the next century. Extensive CO_2 circulation in atmosphere, biological systems, industry and agriculture necessitates the development of novel methods of CO_2 monitoring. Another important and still unresolved issue is chemical fixation of CO_2.[2,3]

CO_2 is generally an unreactive molecule, but it does combine rapidly with amines at ordinary temperatures and pressures to form carbamates. The chemistry between CO_2 and amines is essentially an acid–base equilibrium (Fig. 1).[4] Two molecules of an amine, in presence of CO_2, react to form a carbamic salt, presumably by way of the corresponding carbamic acid. Carbamate anions can be further

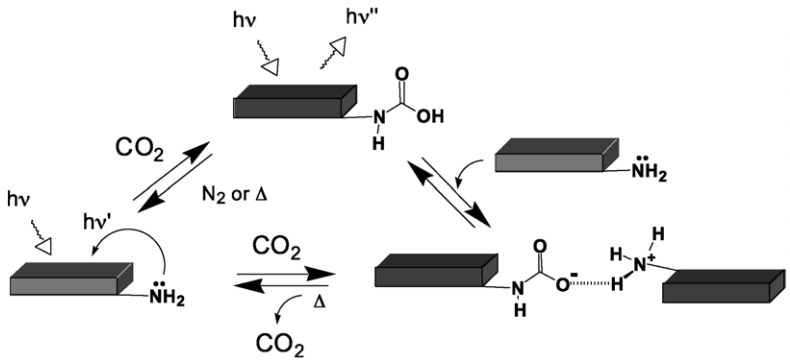

Figure 1. Reversible covalent chemistry between CO_2 and amines.

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converted to isocyanates[5] or may react with alkyl halides to yield urethanes,[4,6,7] thus providing an alternative synthetic equivalent to highly toxic phosgene. Furthermore, carbamates are thermally unstable and release CO_2 upon heating. This can be useful under several circumstances. Polymer-bound amines are employed in industry as reusable 'CO_2 scrubbers,' removing CO_2 from industrial exhaust streams.[8,9] By reacting with amino groups, CO_2 is absorbed into solutions of an amine or an amine-containing ionic liquid.[10] This method has also been extended to use of multiple amine-containing dendrimers.[11] Exposure of solutions of some long-chain alkyl amines to CO_2 results in the reversible formation of organogels.[12] Thermally reversible carbamate chemistry has been recently employed for molecular imprinting of polymers.[13]

Chemical reactions between CO_2 and amines have also been employed for the gas sensing.[14–16] This is for a good reason. Although CO_2 sensing and environmental monitoring is well documented,[17,18] many significant problems remain. One of them is a direct detection. Others[15] and we[16] recently demonstrated the ability of some amines to function as direct and reusable, fluorescent CO_2 sensors (Fig. 1). In this paper, we disclose the chemistry behind these processes and identify the corresponding carbamic acids as the species causing the fluorescence. We provide NMR spectroscopic evidence of the formation of free (!) carbamic acid as an observable intermediate in carbamate formation. Finally, we report on the synthesis and evaluation of CO_2-sensing amino acids for potential use in biocompatible environments. Taken together, our results open more possibilities to detect and chemically utilize CO_2.

2. Results and discussion

2.1. UV–vis and fluorescent spectroscopy

Primary amines **1** and **2**, used in this work, possess naphthalene and pyrene fluorophores, respectively, separated from the NH_2 group by a methylene unit. Bubbling CO_2 for 1–2 h through solutions of 1-(aminomethyl)naphthalene **1** or 1-(aminomethyl)pyrene **2** in polar aprotic solvents such as DMSO and DMF did not affect their UV–vis characteristics, but resulted in dramatic changes in their fluorescence emissions. Specifically, upon excitation of **1** at λ_{ex}=282 nm, the fluorescence emission at λ_{em}=334 nm in DMF increased by more than 10 times (Fig. 2A). The fluorescence at λ_{em}=408 nm of pyrene derivative **2** in DMF increased similarly, at λ_{ex}=341 nm (Fig. 2B).

We found, that the species responsible for the observed fluorescence are the corresponding carbamic acids **3** and **4**. Free amines **1** and **2** only weakly emit fluorescence under ambient conditions. This is due to photo-induced electron transfer (PET) quenching of the excited fluorophore by the intramolecular amino group lone pair. Upon reaction of dissolved CO_2 with amines **1** and **2**, carbamic acids **3** and **4** are formed. PET quenching no longer takes place: the lone pair of electrons on the nitrogen atom is now involved in a conjugation with the carbonyl oxygen. This leads to an overall increase in observed fluorescence. PET of this type is known and has been exploited for pH sensing.[19] In fluorescent pH sensors, protonation of the amine in acidic solutions prevents intramolecular PET from occurring. Bubbling N_2 through solutions of **3** and **4** resulted in loss of fluorescence.

2.2. NMR spectroscopy

Reactions, involving amines **1**, **2**, and CO_2, were then monitored in the NMR tube in DMSO-d_6. The solvent was first purged with dried N_2 before addition of amines. In the presence of dissolved CO_2 (10–15 equiv.), **1** and **2** cleanly and quantitatively reacted to form the corresponding carbamic acids **3** and **4**. These appeared to be reasonably stable and can be studied by ^1H and ^{13}C NMR spectroscopy (Figs. 3 and 4).

Specifically, prior to CO_2 exposure, benzylic protons of **1** and **2** were seen as singlets at 4.19 and 4.46 ppm, respectively. After CO_2 bubbling, these were transformed into doublets (J=6.0 Hz) at 4.63 and 4.91 ppm, respectively. In both cases, a very broad signal appeared at

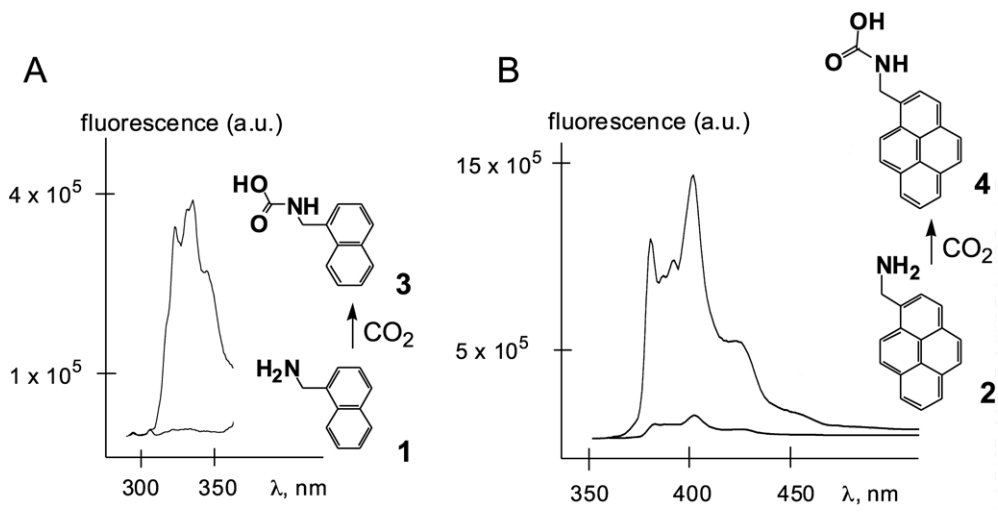


Figure 2. Fluorescence measurements (DMF, 295±1 K) before and after saturation with CO_2 with: (A) aminomethylnaphthalene **1**, λ_{ex}=282 nm; (B) aminomethylpyrene **2**, λ_{ex}=341 nm. All solutions were deoxygenated with N_2 prior measurements. [**1**]=[**2**]=10^{-6} M.

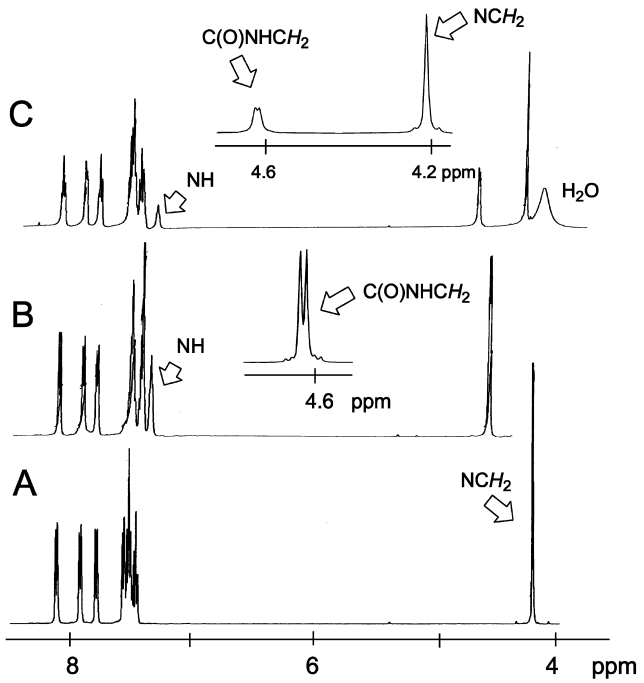


Figure 3. CO_2 induced spectral changes of aminomethylnaphthalene **1**. ^1H NMR spectra (500 MHz, DMSO-d_6, 295 K) of: (A) **1**; (B) **1** after saturation with CO_2; formation of carbamic acid **3**; (C) independently prepared carbamate salt **5**. The NH and benzylic CH_2 signals are marked. The initial solutions were deoxygenated with dried N_2 prior measurements.

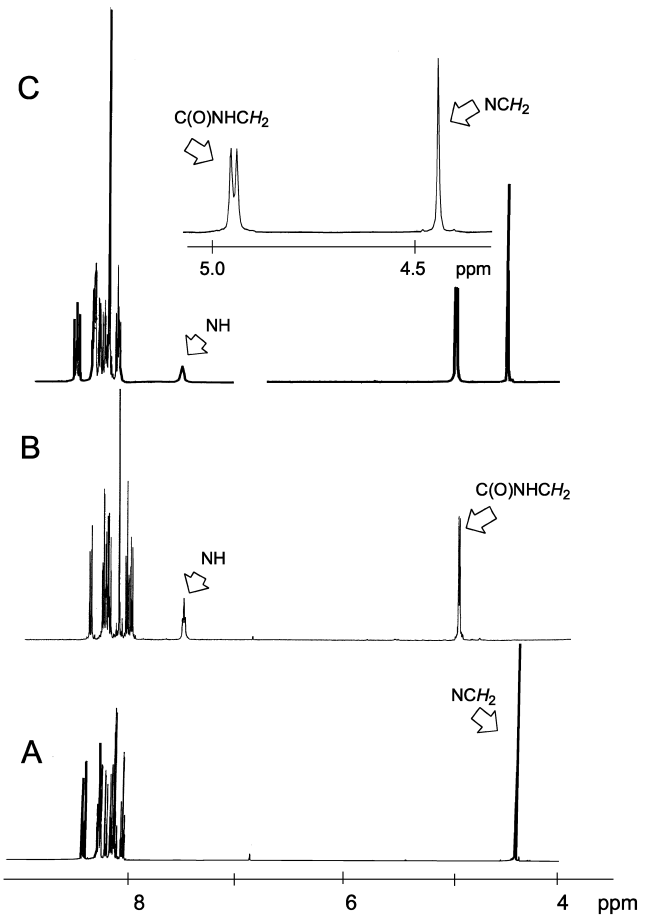


Figure 4. CO_2 induced spectral changes of aminomethylpyrene **2**. ^1H NMR spectra (500 MHz, DMSO-d_6, 295 K) of: (A) **2**; (B) **2** after saturation with CO_2; formation of carbamic acid **4**; (C) independently prepared carbamate salt **6**. The NH and benzylic CH_2 signals are marked. The initial solutions were deoxygenated with dried N_2 prior measurements.

~10.6 ppm, which was assigned to the C(O)*OH*. The carbamate NH signals also emerged as triplets (J=6.0 Hz) at 7.37 and 7.54 ppm, respectively. Furthermore, resonances at ~158 ppm in the ^{13}C NMR spectra of **3** and **4** identified the carbamic (C=O) carbon atom.

Bubbling N_2 through these solutions resulted in loss of CO_2 from some carbamic acid molecules to form the free amines **1** or **2**, which then quickly abstracted a proton from remaining carbamic acid. Alkylammonium carbamic salts **5** and **6** partially precipitated from solution. Further CO_2 loss cannot be achieved by prolonged bubbling of N_2, but the carbamic salts can lose CO_2 at elevated temperatures to reform the amines **1** and **2**, and this was in fact achieved by brief reflux in toluene.

The identities of the precipitated salts were confirmed by comparison to separately prepared samples of the salts **5** and **6** (Fig. 5). These samples were prepared by bubbling CO_2 through solutions of **1** and **2** in a less polar solvent such as $CHCl_3$ or MeCN. ^1H NMR, ^{13}C NMR, and CHN elemental analysis confirmed the structure and composition of the salts **5** and **6**. For instance, benzylic protons were seen in DMSO-d_6 as two separate signals in their ^1H spectra: a singlet at 4.22 and a doublet at 4.62 ppm (J=5.5 Hz) for **5**, and a singlet at 4.48 and a doublet at 4.90 ppm (J=5.5 Hz) for **6**. The carbamate NH signals were seen as triplets (J=5.5 Hz) at 7.32 and 7.53 ppm, respectively. A resonance at 158 ppm in the ^{13}C NMR spectrum of **5** identified the carbamic (C=O) carbon atom.

Carbamic acids, with $NH_2C(O)OH$ as a simplest representative, have been the subject of considerable speculation and are still elusive. These are often suggested as intermediates in the decomposition of carbamates, hydrolysis of isocyanates, in the Hofmann and Curtius rearrangements. There is little direct evidence, however, to support this. Up to now, carbamic acids were thought to be highly unstable and have only been observed by somewhat unconventional methods. Composite ices of NH_3, H_2O, and CO_2 have been studied by IR, suggesting the formation of carbamic acid upon irradiation with a 1 MeV proton source.[20] Several protonated carbamic acids have been characterized by Olah and co-workers under superacidic conditions.[21] In a spectacular case, the solid-state structure of dibenzylamine carbamic acid was published.[22] However in solution, prior

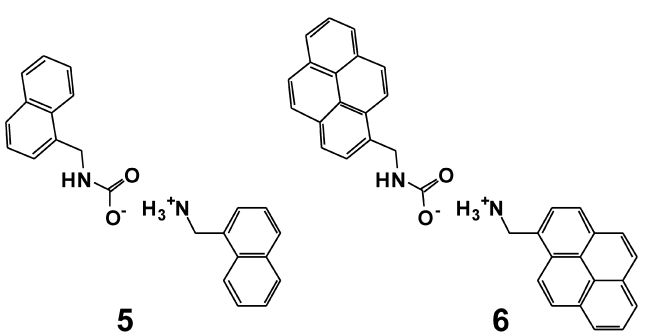


Figure 5. Carbamic salts **5** and **6**.

to our studies, no free carbamic acids had been observed. Chemistry of carbamic acids is important, since they may form in biological systems in presence of CO_2. Our results indicate that facile atmospheric control can allow the observation and study of carbamic acids using conventional spectroscopic techniques such as NMR and fluorescence spectroscopy.

2.3. A CO_2-sensing amino acid

For potential application in sensing, receptor molecules must not only be preparatively available, but also readily immobilizable on other (macro)molecules, solid supports, or surfaces. Importantly, they should also be properly configured to sufficiently respond to the presence of an analyte. Existing literature protocols on synthesis of naphthalenes and pyrenes, containing two or more functional groups, typically require many steps and are time-consuming. Aminomethyl naphthalenes and pyrenes containing other functional fragments are not known. Following the natural strategy to employ amino acids as universal building blocks for a huge variety of proteins and enzymes, we identified α-naphthylglycine **7** (Scheme 1) as an immobilizible CO_2-sensing module. Indeed, similar to **1** and **2**, structure **7** contains aminomethyl units attached to the fluorescently active aromatic fragment. At the same time, the carboxylic groups in **7** can be effectively used for further attachments and/or incorporation into larger macrostructures. For example, it can react with commercially available polymeric supports such as chloromethyl, hydroxymethyl or aminomethyl polystyrenes, or be incorporated within the oligopeptide nanostructures.

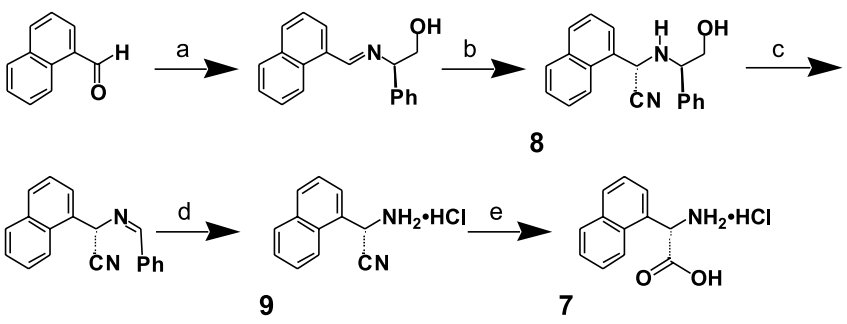
The simplest route to α-arylglycines is through the racemic Strecker synthesis, known in the literature for over a century.[23] While racemic synthesis is both cost and time efficient, it may prove useful for future biological applications to acquire enantiomerically pure biocompatible structures, particularly if they can be used to monitor enzyme–CO_2 interactions. Modifications of the Strecker procedure employ a chiral auxiliary to induce diastereoselectivity in an intermediate. The chiral auxiliary can be further removed to yield the enantiomerically enriched amino acid. Thus, the method chosen here reflects consideration for experimental ease and a high yield of enantio-enriched products.

In the synthesis of **7** we initially followed the diastereoselective Strecker method (Scheme 1), recently reported by Hosangadi and Dave.[24] In short, reaction of 1-naphthaldehyde with (*R*)-2-amino-2-phenylethanol in $CHCl_3$, followed by addition of trimethylsilylcyanide (TMSCN), generated the intermediate **8** with a diastereomeric yield [(*S*,*R*)–(*R*,*R*)] of 84:16, determined by integration of the α-methine proton in the ^1H NMR spectrum. The (*S*,*R*)-**8** diastereomer was further purified by successive recrystallizations from EtOAc/hexanes, 1:4. This procedure provided (*S*,*R*)-**8** with >98% diastereomeric purity by ^1H NMR. After oxidative cleavage of formaldehyde by $Pb(OAc)_4$, hydrolysis of the imine was attempted by stirring in 6 M HCl, as reported,[24] at rt for 1 h, followed by stirring at 90°C for 1 h. The FTIR and ^{13}C NMR spectral analysis of the crude product revealed, however, that the nitrile functional group still remains. A carbon resonance at ~116 ppm was assigned for the nitrile, and the resonance for a carboxylic acid was not found. Accordingly, not acid **7**, as reported earlier,[24] but instead nitrile **9** was formed under these conditions. This compound was further unambiguously characterized by FTIR, ^1H and ^{13}C NMR spectroscopy and CHN elemental analysis.

Obviously, while it is easy to cleave the imine, more effort is needed to hydrolyze the nitrile group. After several optimization experiments, we found that vigorous treatment of **9** with concentrated HCl in a sealed vessel for 4 h at 90°C resulted in 70% formation of 1-naphthylglycine **7** as a hydrochloric salt.

Sensing experiments, similar to those for **1** and **2**, were performed for **7** in D_2O and DMSO-d_6, in the presence of triethylamine (TEA). Addition of TEA effected neutralization of the hydrochloric salt of **7**, and as well prevented protonation of the amino group. Control experiments confirm that TEA does not react with CO_2 and its presence is innocuous. Upon exposure to CO_2, the fluorescent response of **7** was similar to that of **1**, showing an enhancement of monomer emission by four to five times in water or DMSO solution (Fig. 6).[25]

When followed by ^1H NMR spectroscopy in D_2O, the α-methine signal of **7** was seen as a singlet at 5.04 ppm prior to CO_2 bubbling. After bubbling CO_2 for 5 h, the methine proton signal was shifted downfield to 5.52 ppm. In addition, the aromatic region of the spectrum totally changed (Fig. 7). These spectral data are in agreement with observations recorded for amines **1** and **2**, so at this stage we conclude that the carbamate formation definitely takes place with **7** in aqueous solution. The fate of the corresponding carbamic acid is not clear and requires more



Scheme 1. Diastereoselective Strecker synthesis of (*S*)-α-naphthylglycine **7**: (a) *R*-2-amino-2-phenylethanol, $CHCl_3$, rt, 4 h. (b) TMSCN, $CHCl_3$/MeOH, rt, 24 h, 76% (two steps). (c) $Pb(OAc)_4$, CH_2Cl_2/MeOH, 20 min. (d) 6 M HCl, rt, 1 h, 90°C, 45 min, >95% (two steps). (e) 6 M HCl, 90°C, 4 h, 70%.

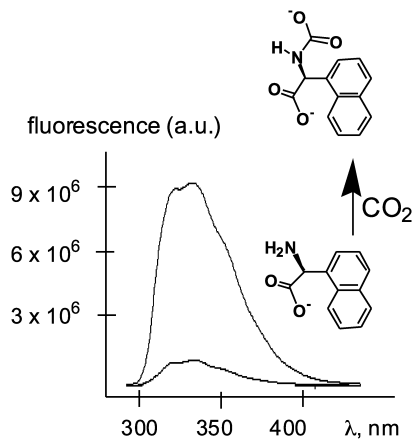


Figure 6. Fluorescence measurements with naphthylglycine **7** (4 equiv. TEA, H_2O, 295±1 K) before and after saturation with CO_2. λ_{ex}=282 nm; [**7**]=10^{-6} M.

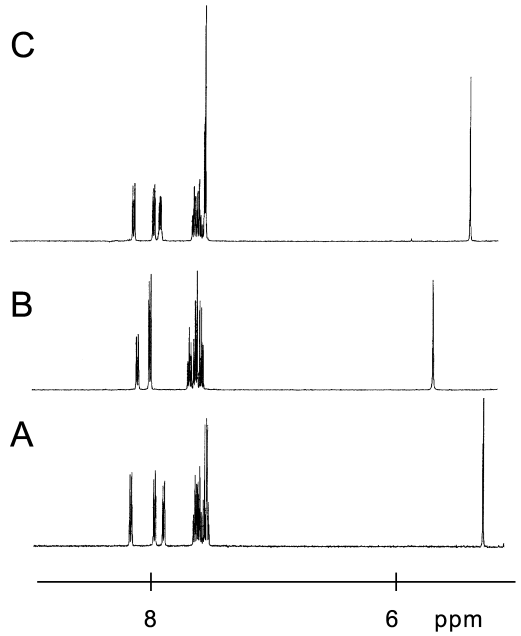


Figure 7. CO_2 induced spectral changes of naphthylglycine **7**. ^{1}H NMR spectra (500 MHz, D_2O, 4 equiv. TEA, 295 K) of: (A) **7**; (B) **7** after saturation with CO_2; (C) solution B after purging with N_2 at 70°C for 1 h.

detailed studies. The acidic proton is, most probably, transferred to a TEA molecule (pK_a (Et_3N^+H)~10.75), thus generating the corresponding carbamic anion (Fig. 6). This is a well-known scenario for carbamate salts formation in the presence of a base.[4–14] Subsequent bubbling of N_2 for 3 h did not reverse the process. The amino acid **7** was however recovered by purging with N_2 at 70°C for 1 h (Fig. 7).

These experiments confirm the capability of this unnatural amino acid to form carbamates in the presence of dissolved CO_2, and as such identify **7** as a possible CO_2 sensor.[26]

3. Conclusions and outlook

The simple chemistry between CO_2 and amines can be used to directly detect dissolved CO_2 in polar solution through the PET quenching effect. Free carbamic acids of amines can be observed by NMR and fluorescence spectroscopy in solution. The identification and evaluation of naphthylglycine as a CO_2-sensitive module widens possibilities for working in aqueous solution with an optical response and also for immobilization and incorporation into natural nanoscaffolds.

4. Experimental

4.1. General

Melting points were determined on a Mel-Temp apparatus (Laboratory Devices, Inc.) and a Buchi apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 295±1 K, unless stated otherwise, on JEOL Eclipse 500 MHz spectrometer. Chemical shifts were measured relative to residual non-deuterated solvent resonances. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer. UV–vis spectra were measured on a JASCO V-530 spectrophotometer. Fluorescence studies were performed on a Jobin Yvon Fluoromax 3 spectrometer. Elemental analysis was performed on a Perkin–Elmer 2400 CHN analyzer. For column chromatography, Silica Gel 60 Å (Sorbent Technologies, Inc.; 200–425 mesh) was used. All experiments with moisture- or air-sensitive compounds were run in freshly distilled, anhydrous solvents under a dried nitrogen atmosphere.

4.1.1. Aminomethylnaphthyl carbamic acid 3. ^{1}H NMR (DMSO-d_6): δ=10.60 (bs, 1H), 8.13 (d, J=7.5 Hz, 1H), 7.94 (d, J=7.5 Hz, 1H), 7.83 (d, J=7.5 Hz, 1H), 7.6–7.4 (m, 4H), 7.37 (t, J=6.0 Hz, 1H), 4.62 (d, J=6.0 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ=158.1 (C=O), 136.0, 133.8, 131.4, 129.1, 127.9, 126.7, 126.3, 126.0, 125.4, 124.0, 42.4.

4.1.2. Aminomethylpyrenyl carbamic acid 4. 1-(Aminomethyl)-pyrene hydrochloride (0.268 g, 1 mmol) was shaken in THF (15 mL) with 10% NaOH (15 mL) in a separatory funnel. The organic layer was separated, dried (Na_2SO_4) and evaporated. ^{1}H NMR (DMSO-d_6): δ=8.5–8.0 (m, 9H), 7.54 (t, J=6.0 Hz, 1H), 4.91 (d, J=6.0 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ=158.1 (C=O), 134.0, 131.3, 130.8, 130.5, 128.3, 128.1, 127.9, 127.5, 126.9, 126.7, 125.8, 125.7, 125.3, 124.7, 124.5, 124.4, 123.6, 42.5.

4.1.3. 1-(Aminomethyl)-naphthalene ammonium carbamate 5. CO_2 gas was bubbled through a solution of 1-(aminomethyl)-naphthalene **1** (0.47 mL, 3.2 mmol) in $CHCl_3$ (10 mL) for 15 min. The white precipitate was filtered and dried in vacuo. Yield >95%; mp 105°C (decomp.); ^{1}H NMR (DMSO-d_6): δ=8.12 (t, J=6.5 Hz, 2H), 7.93 (d, J=7.3 Hz, 2H), 7.81 (t, J=7.3 Hz, 2H), 7.6–7.4 (m, 8H), 7.32 (t, J=5.5 Hz, 1H), 4.62 (d, J=5.5 Hz, 2H), 4.22 (s, 2H); ^{13}C NMR (DMSO-d_6): δ 158.5 (C=O), 139.4, 136.3, 133.8, 131.5, 131.4, 129.0, 127.8, 127.4, 126.6, 126.5, 126.2, 126.14, 126.10, 126.0, 125.3, 125.0, 124.1, 124.0, 43.3, 42.4. Anal. calcd for $C_{23}H_{22}N_2O_2$·0.2H_2O: C, 76.30; H, 6.24; N, 7.74. Found: C, 76.20; H, 6.59; N, 7.76.

4.1.4. 1-(Aminomethyl)-pyrene ammonium carbamate 6. 1-(Aminomethyl)-pyrene hydrochloride (0.268 g, 1 mmol)

was shaken in THF (15 mL) with 10% NaOH (15 mL) in a separatory funnel. CO_2 was then bubbled through the organic layer for 15 min. The off-white precipitate was filtered and dried in vacuo. Yield >95%; mp 80–95°C (decomp.); ^{1}H NMR (DMSO-d_6): δ=8.5–8.0 (m, 18H), 7.53 (t, J=5.5 Hz, 1H), 4.90 (d, J=5.5 Hz, 2H), 4.48 (s, 2H). Anal. calcd for $C_{35}H_{26}N_2O_2$: C, 82.98; H, 5.17; N, 5.53. Found: C, 83.03; H, 5.47; N, 5.35.

4.1.5. (*S*,*R*)-2-[(2-Hydroxy-1-phenylethyl)amino]-2-(1-naphthyl)ethanenitrile 8. A solution of 1-naphthaldehyde (1.36 mL, 10 mmol) and (*R*)-2-phenylglycinol (2.0 g, 15 mmol) in $CHCl_3$ (35 mL) was stirred in presence of 4 Å molecular sieves at rt in air for 4 h. The solvent was removed at reduced pressure to leave a pale-yellow oil, which was then redissolved in $CHCl_3$ (20 mL) and MeOH (3 mL). The solution was cooled to 0°C and trimethylsilylcyanide (2.8 mL, 20 mmol) was added slowly by syringe. The mixture was then allowed to stir for 24 h at rt. The solvents were removed at reduced pressure to afford crude **8** as an yellow oil that crystallized upon standing. The solids were recrystallized twice from EtOAc–hexanes, 1:4 (20 mL) and separated by vacuum filtration to give a shiny off-white powder (2.29 g, 76%): mp 120–122°C; ^{1}H NMR ($CDCl_3$): δ=8.85 (m, 3H), 8.7 (m, 1H), 8.4–8.6 (m, 8H), 5.11 (s, 1H), 4.35 (dd, J=9.5, 4.5 Hz, 1H), 3.84 (dd, J=11, 4.5 Hz, 1H), 3.68 (t, J=10 Hz, 1H), 2.58 (br s, 1H), 1.77 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 138.1, 134.0, 130.7, 130.3, 130.2, 129.1, 129.0, 128.9, 128.3, 126.9, 126.3, 126.0, 125.4, 123.0, 118.9, 67.0, 63.8, 50.1. Anal. calcd for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.34; H, 5.94; N, 9.27.

4.1.6. (*S*)-α-1-Naphthylglycine 7. A mixture of **8** (1.5 g, 5 mmol) in CH_2Cl_2 (20 mL) and MeOH (10 mL) were stirred to dissolve. After cooling to 0°C, lead tetraacetate (2.22 g, 5 mmol) was added in one portion, darkening the solution from pale yellow to orange. After stirring for 20 min, saturated aqueous $NaHCO_3$ (50 mL) was added in portions with swirling. Insoluble impurities were removed by filtration over Celite and washed with CH_2Cl_2 (50 mL). The filtrate was extracted with CH_2Cl_2 (2×10 mL), dried over Na_2SO_4 and evaporated at reduced pressure to leave a yellow oil, which was subjected to hydrolysis without purification. Several attempts to reproduce the published procedure[22] for the hydrolysis, employing 6 M HCl at rt for 1 h, and then at 90°C for 45 min, resulted only in nitrile **9** as a hydrochloric salt. Yield >95%; mp 180°C (decomp.); ^{1}H NMR (D_2O): δ=8.10 (m, 3H), 7.90 (d, J=7 Hz, 1H), 7.7 (m, 3H), 6.52 (s, 1H); ^{13}C NMR (D_2O): δ=133.8, 132.2, 129.5, 129.1, 128.3, 127.4, 127.3, 125.6, 124.0, 121.6, 115.6, 41.9; FT-IR (oil mull, cm^{-1}, HCl salt): ν=2364 (CN). Anal. calcd for $C_{12}H_{11}N_2Cl$: C, 65.90; H, 5.03; N, 12.81. Found: C, 65.98; H, 5.35; N, 12.91.

In the modified procedure, a suspension of the oil in concentrated HCl (10 mL) was stirred at 90°C in a sealed vessel. The solids dissolved at temperatures greater than 80°C and then began to precipitate as the amino acid salt began to form after ~1 h. After 4 h of stirring, the mixture was cooled to 0°C and solids were filtered and washed with small portions of cold H_2O, followed by cold ether to yield (*S*)-α-1-naphthylglycine hydrochloride **7** as a white powder (0.828 g, 70%): mp >250°C; $[\alpha]_D^{23}$=+155 (c=1.0, 1 M HCl) [lit.[24] $[\alpha]_D^{20}$=+166 (c=1.0, 1 M HCl)]; ^{1}H NMR (D_2O, Et_3N): δ=8.18 (d, J=7.5 Hz, 1H), 8.9 (m, 2H), 8.55 (m, 4H), 5.04 (s, 1H); ^{1}H NMR ([D_6]DMSO-d_6, Et_3N): δ=8.32 (d, J=8 Hz, 1H), 8.9 (m, 2H), 7.5–7.6 (m, 4H), 5.03 (s, 1H); ^{13}C NMR (D_2O, Et_3N): δ 181.5, 138.6, 133.9, 130.9, 129.0, 128.1, 126.7, 126.1, 126.0, 123.7, 57.8; FTIR (KBr, $^{-1}$, HCl salt): ν=3425, 2989, 1733, 1599, 1497. Anal. calcd for $C_{12}H_{12}NCl$: C, 60.64; H, 5.09; N, 5.89. Found: C, 60.34; H, 5.30; N, 6.26.

4.2. Fluorescence measurements

Fluorescence measurements were performed at 295±1 K using solvents that had been previously degassed with dried N_2. All fluorescence spectra were recorded at 10^{-6} M concentration. The excimer emission was seen at $>10^{-4}$ M. Solutions of **7** were prepared by dilution of a stock solutions of **7** (10^{-3} M) and TEA (10^{-2} M).

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USA, however, are nonchemical and are mostly in refrigeration and beverage industries. Totally, only 0.7–1.0% of the produced CO_2 is used, and the consumption in chemical industries is ~0.1%.

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