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Supramolecular Structures from Lysine Peptides and Carbon Dioxide

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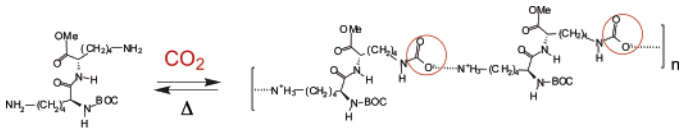

peptide-based supramolecular polymers

The design, synthesis, and characterization of novel linear and cross-linked supramolecular polymers that are easily available from biologically friendly lysine peptides and carbon dioxide (CO_2) are reported here. Polymeric structures **5**, **6**, and **19** readily form from peptides **2**, **3**, and **15**, respectively, at ambient temperatures by simply bubbling CO_2 through their solutions in apolar organic solvents ($CHCl_3$, benzene) and even in the presence of 10% MeOH. The resulting gels can be easily isolated from solution, dried, and stored refrigerated for several months. At the same time, they may thermally release CO_2 and convert back to the corresponding monomers. As a consequence, their structures and physical properties are switchable. They may also trap, store, and release foreign molecules. The typical entrapment procedure was demonstrated for tripeptide **3**, CO_2, and the commercially available dye coumarin 2.

Introduction

Supramolecular polymers represent a novel class of macromolecules, in which monomeric units are held together by reversible forces.[1] Supramolecular polymers thus combine features of conventional polymers with properties resulting from the bonding reversibility. The degree of polymerization, lifetimes, physical properties, and architectures of supramolecular polymers can be switched "on−off" through the main chain self-assembly−dissociation processes. We recently proposed to build supramolecular polymers using dynamic, reversible chemistry between carbon dioxide (CO_2) and primary amines (Figure 1).[2] Carbamate bridges between monomers readily form by simply bubbling CO_2 through solutions of amines in apolar solvents. Being robust and stable, they, however, release CO_2 upon gentle heating and transform back to the amines. In this paper, we report on the design, synthesis, and characterization of novel supramolecular polymers and cross-linked 3D materials that are based on peptides. Fabrication of molecular materials using simple and versatile peptide construction motifs is a quickly emerging area in bio(nano)technology.[3] We show that short lysine peptides reversibly react with CO_2 to form polymeric assemblies. These are stable under laboratory conditions but may thermally release CO_2 and convert back to the monomers. As a consequence, their structures and physical properties are switchable. They also may trap, store, and release foreign molecules under thermal control. Accordingly, our work opens novel perspectives for the design of switchable supramolecular materials for molecular storage and other applications.

Results and Discussion

Design. CO_2 is known to rapidly react with amines at ordinary temperatures and pressures to form carbamate salts.[4] Their

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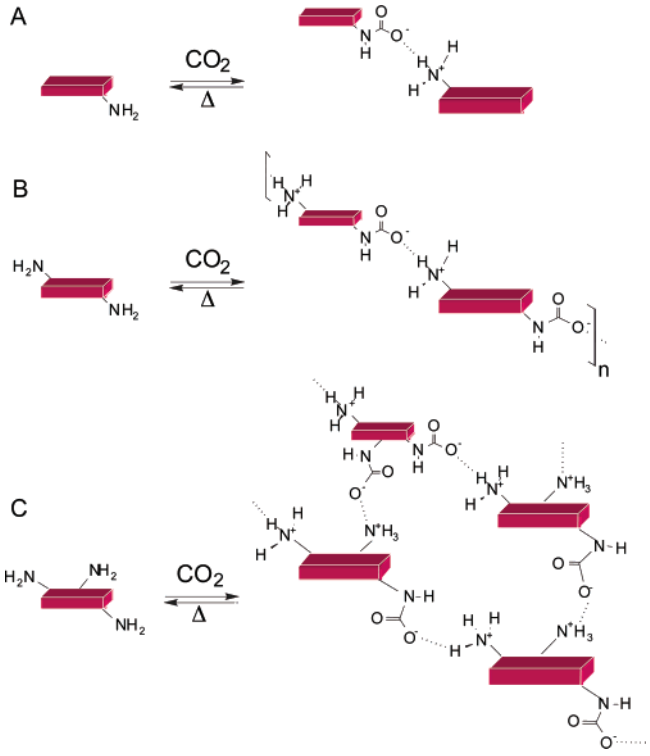

FIGURE 1. Design of carbamate-based linear and cross-linked supramolecular (reversible) polymers from CO_2.

formation is thermally reversible. This chemistry has been utilized in amine-based "CO_2 scrubbers"[5] and also for the preparation of organogels.[6] While reactions between CO_2 and amino acids have been known for years,[7] this has never been used for the construction of novel materials.[8] In this work, peptide monomers **1**−**3** were designed, which (a) are readily available either from commercial sources or via two or three synthetic steps, utilizing conventional peptide chemistry, (b) are chiral, (c) are biologically friendly, (d) can be easily functionalized on the periphery, and (e) possess terminal CO_2-philic primary amino groups and, therefore, can react with CO_2 in apolar solution.

The approach is sketched in Figure 2 and introduces linear and cross-linked lysine-based supramolecular structures **4**−**6**. Simple Boc-(*L*)-Lys-NHPr (**1**) was selected as a model compound. It served to verify the reactivity of a primary ϵ-NH_2 group with CO_2 and also to allow us to obtain characteristic NMR data for lysine-based carbamates. The molecular modeling[9] results show that Boc-(*L*)-Lys-(*L*)-Lys-OMe dipeptide **2** represents an ideal unit for the construction of the linear supramolecular polymer **5**. As shown in Figure 3A, both of its free ϵ-NH_2 groups are pointing to opposite directions, thus allowing the formation of a chainlike carbamate structure.

Similarly, Boc-(*L*)-Lys-(*L*)-Lys-(*L*)-Lys-OMe tripeptide **3**, having three free ϵ-NH_2 groups, enables the construction of three-dimensional carbamate **6** after reaction with CO_2. Figure 3B shows that carbamate **6** possesses a quite developed porous structure with 20−25 Å pores. Such cross-linked supramolecular polymers may be suitable for the encapsulation of various guests.

Synthesis (Scheme 1). Boc-(*L*)-Lys-NHPr (**1**) was synthesized from commercially available Boc-(*L*)-Lys(Cbz)-OH (**7**) and *n*-propylamine in the presence of EDCI·HCl and HOBt in CH_2Cl_2, followed by the cleavage of the Cbz protecting group by Pd/C and H_2 in MeOH, in overall ∼85% yield. Similarly, lysine dipeptide **10** was prepared from commercially available Boc-(*L*)-Lys(Cbz)-OH (**7**) and (*L*)-Lys(Cbz)-OMe·HCl (**9**), using EDCI·HCl and HOBt as peptide coupling agents, in 85% yield. Derivative **10** was further used for the synthesis of both lysine tripeptide **3** and bridged lysine dipeptide **15**. First, **10** was treated with in situ-generated HCl (from AcCl in MeOH) to cleave the Boc protective group, which gave the corresponding ammonium salt **11** in 91% yield. This was then coupled with Boc-(*L*)-Lys(Cbz)-OH (**7**) under the same conditions as described above to give Boc-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-OMe (**12**) in 82% yield. Finally, the cleavage of the Cbz protective group (H_2, Pd/C, MeOH) offered Boc-(*L*)-Lys-(*L*)-Lys-(*L*)-Lys-OMe (**3**) in a quantitative yield.

To further increase the number of reactive amino groups, we again employed the above-mentioned lysine dipeptide and designed a building block bearing two relatively distant pairs of reactive amino groups. We expected that the presence of a sufficiently long spacer between both lysine dipeptide subunits could have a significant influence on the size and shape of the pores in the interior structure. To obtain bridged dipeptide **15**, Boc-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-OMe (**10**) was initially hydrolyzed under basic conditions (aq NaOH). The resulting carboxylic acid **13** was then coupled with 1,12-diaminododecane to give the protected bridged dipeptide **14** in 90% yield. This was finally treated with Pd/C under H_2 atmosphere to give **15** in a quantitative yield.

Syntheses of Lysine-Based Carbamates and Their NMR Study. CO_2 quantitatively reacts with simple lysine derivative **1** upon bubbling though the DMSO-d_6 solution with the formation of carbamic acid **16** (Scheme 2, Figure 4). The acid is quite stable in solution and was characterized by ^1H, ^{13}C, and $^1H-^1H$ COSY NMR spectroscopy. The appearance of a new triplet at 6.65 ppm, belonging to the −N*H*C(O)OH protons, and a significant shift of the corresponding α-CH_2 methylene protons to the lower field of 2.88 ppm in the ^1H NMR spectrum, together with a new carbonyl signal at 158 ppm in the ^{13}C NMR spectrum, represent clear evidence for carbamic acid formation. It is noteworthy that free carbamic acids are still very rare and can be seen only in polar aprotic solvents, when larger quantities of CO_2 are used.[4,10]

On the contrary, the use of an apolar aprotic solvent, such as $CHCl_3$, directly leads to the formation of the corresponding

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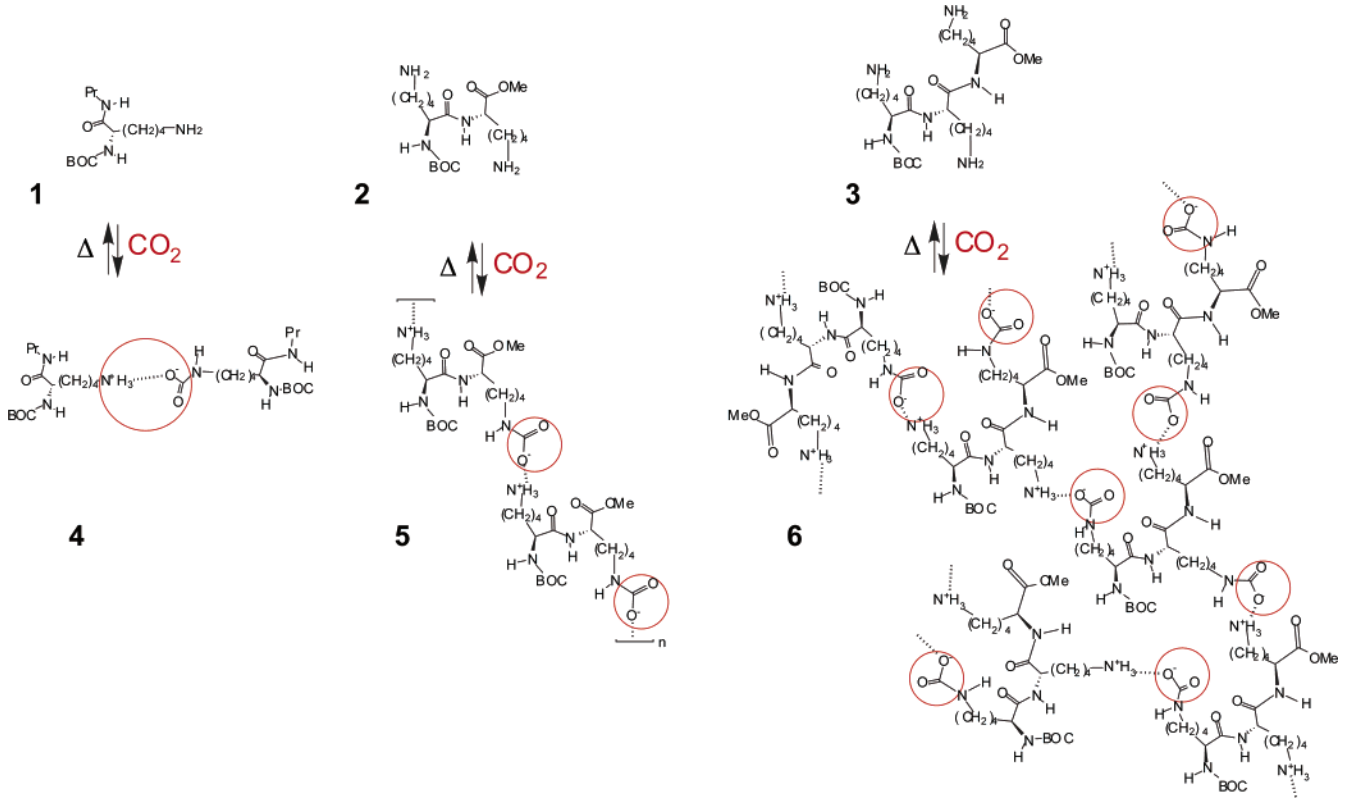

FIGURE 2. Design of (*L*)-lysine-based supramolecular polymers using CO_2 as a linking agent.

ammonium carbamate salt **4** (Figure 2). Upon bubbling CO_2 directly into the solution of **1** in $CDCl_3$ ([**1**] = 1 M), lysine-based carbamate **4** was obtained in a quantitative yield (^{1}H NMR, Figure 5). Compound **4** was also prepared by the bubbling of CO_2 in nondeuterated $CHCl_3$, followed by removal of the solvent under reduced pressure at room temperature (Figure 4). Finally, the solution of **1** in benzene−MeOH (10:1) also reacted with CO_2.[11] The solvent was subsequently removed under reduced pressure at room temperature, affording the same compound **4**.

The ^{1}H NMR spectrum of carbamate **4**, prepared from **1** and CO_2 in $CDCl_3$, clearly shows two 1:1 signals at 2.74 and 2.94 ppm, which correspond to two different α-C*H*$_2$N methylene groups from the carbamate and ammonium ends (Figure 5B). The spectrum also shows two pairs of signals corresponding to the amide and BOC-carbamate NH protons. This feature was not seen in DMSO-d_6, where the carbamate salt is solvated and dissociated.

When measured in DMSO-d_6, the ^{1}H NMR spectrum of carbamate **4** shows the nonequal intensities of the signals at 2.55 and 2.83 ppm, which were assigned as two different α-C*H*$_2$N methylene groups (Figure 4C). A broad signal at ∼5.3 ppm, which most probably belongs to the ammonium N*H*$_3^+$ protons, was found to be concentration dependent. Upon increasing the concentration, it shifts downfield. At 0.05 M, this signal was observed at 4.1 ppm, at 0.2 M, it was shifted to 5.34 ppm, and finally, at 0.5 M, it was present at 6.00 ppm. On the other hand, the broad carbamate-C(O)N*H* signal showed only a slight concentration dependence and moved in an opposite manner from 6.56 (0.05 M) to 6.19 (0.5 M) with increasing concentration. Both the ammonium and carbamate amide signals, along with other amide N*H* protons in the molecule, disappeared upon addition of several drops of D_2O.

To further prove the carbamate salt formation, ^{13}C-labeled CO_2 ($^{13}CO_2$) was bubbled through the solution of **1** in benzene−MeOH (10:1) after which carbamate **4**, labeled with the ^{13}C-carbonyl group, was isolated.[12] Its structure was confirmed by 1D and 2D NMR measurements, ^{13}C NMR spectroscopy, and also ^{1}H−^{13}C HMBC (heteronuclear multibond correlation) spectra (Figure 6). Clear evidence for the N−C covalent bond formation between the amine nitrogen and the $^{13}CO_2$ carbon was obtained. For example, a strong signal for the ^{13}C-labeled carbamate carbonyl group appeared, as expected, at 160.3 ppm and showed a cross-peak with the α-C*H*$_2$ methylene protons at 2.83 ppm in the HMBC spectrum.

Carbamate **4** was found to be quite stable when stored in $CDCl_3$ and refrigerated for 4 months. The reversibility of carbamate formation was proven by simple heating of an NMR

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(11) No significant amounts of alkylammonium bicarbonates were found in cases when benzene−MeOH (10:1) was used. This was concluded from the analysis of the corresponding ^{1}H NMR, ^{13}C NMR, and ^{1}H−^{13}C HMBC spectra. The compounds obtained in benzene−MeOH (10:1) were identical to those obtained using $CHCl_3$ ($CDCl_3$) solutions. For the discussion, see: Ito, Y.; Ushitora, H. *Tetrahedron* **2006**, *62*, 226−235.

(12) When regular CO_2 was used in such experiments, a much weaker ^{13}C carbamate signal was detected, which may be due to partial dissociation of carbamate derivatives to free amine and CO_2 in DMSO solution. For the detailed discussion, see ref 4c.

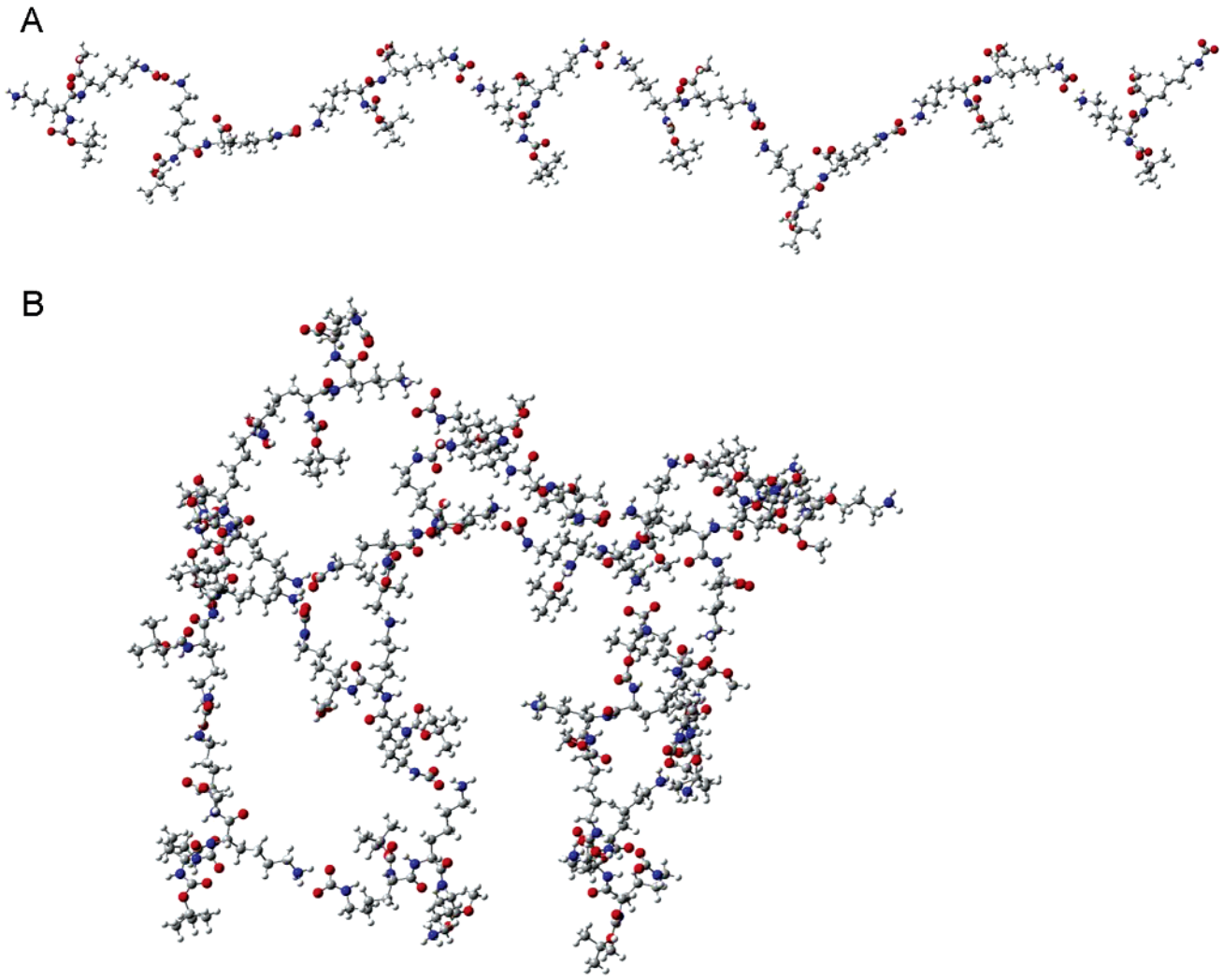


FIGURE 3. (A) Molecular model of the Boc-(*L*)-Lys-(*L*)-Lys-OMe-based carbamate linear polymer **5**. Seven monomer units are shown. (B) Molecular model of the Boc-(*L*)-Lys-(*L*)-Lys-(*L*)-Lys-OMe-based carbamate cross-linked polymer **6**. Fourteen monomeric units are depicted. MacroModel 7.1; Amber* Force Field.[9]

tube containing carbamate **4** in DMSO-d_6 to ~100 °C and simultaneous bubbling of N_2 through this solution for 1 min. The ^{1}H NMR spectrum obtained after the reversal of carbamate formation was identical to that of the starting "free" amine **1**.

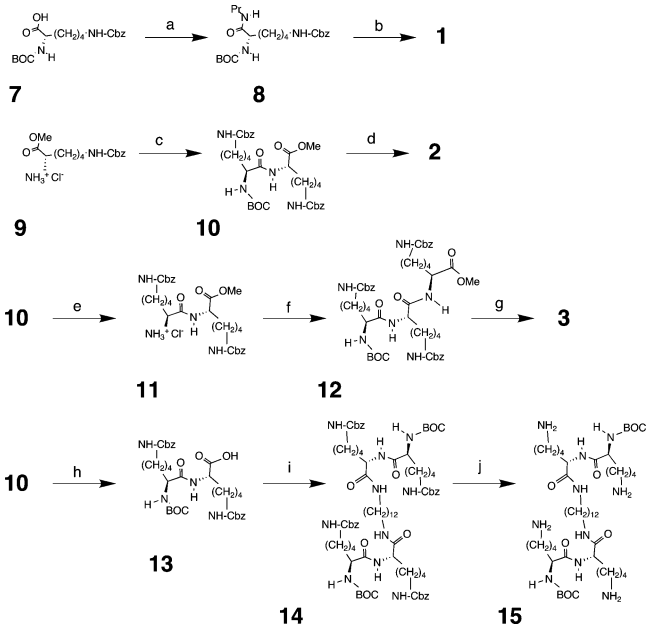
Likewise, lysine dipeptide **2** readily reacts with CO_2 in DMSO-d_6 with the quantitative formation of carbamic acid **17** (Scheme 2). The appearance of a multiplet at 6.66 ppm, belonging to both −N*H*C(O)OH protons, and the pronounced shift of α-CH_2 methylene protons to a lower field of 2.88 ppm, together with a new carbonyl signal at 158 ppm, represent unambiguous evidence of carbamic acid formation (see Figure 7B). Dipeptide **2** was found to be well soluble (up to 1.2 M) in $CHCl_3$, but when CO_2 was bubbled through the solution of **2** in $CHCl_3$ (0.15−1.2 M concentration range), the corresponding carbamate **5** formed as a colorless gel. After removal from the solution, gel **5** quickly turned into a white powder.

Product **5** is insoluble in most apolar aprotic solvents, and NMR measurements were performed in DMSO-d_6, where carbamate **5** exists in equilibrium with the corresponding carbamic acid **17** and "free" amine **2**.[4c] In contrast to the starting lysine dipeptide **2**, carbamate **5** showed two different signals at a 1:1 ratio for the α-CH_2 methylene protons (Figure 7C). The appearance of new broad signals at ~6 ppm, corresponding to the carbamate N*H* and ammonium NH_3^+ protons, respectively, represents additional structural evidence for **5**. The position of the broad NH_3^+ signal was found to be concentration dependent. It moves downfield upon increasing the concentration.

The carbamate formation was also evident from the ^{13}C NMR and HMBC experiments, where ^{13}C-labeled CO_2 was used.[12] As shown in Figure 8B,C, a very intene signal for the ^{13}C-labeled carbamate carbonyl group appeared, as expected, at 160.9 ppm and gave a strong cross-peak with the α-CH_2 methylene protons at 2.85 ppm in the HMBC spectrum. This proves the N−C bond formation between the amine nitrogen in **5** and the $^{13}CO_2$ carbon. Solid carbamate **5** was found to be stable when stored refrigerated for at least 4 months. The carbamate bonds can, however, be broken by heating to ~100 °C and simultaneous bubbling of N_2 through the solution. The ^{1}H NMR spectrum obtained after such treatment was identical to that of starting amine **2**.

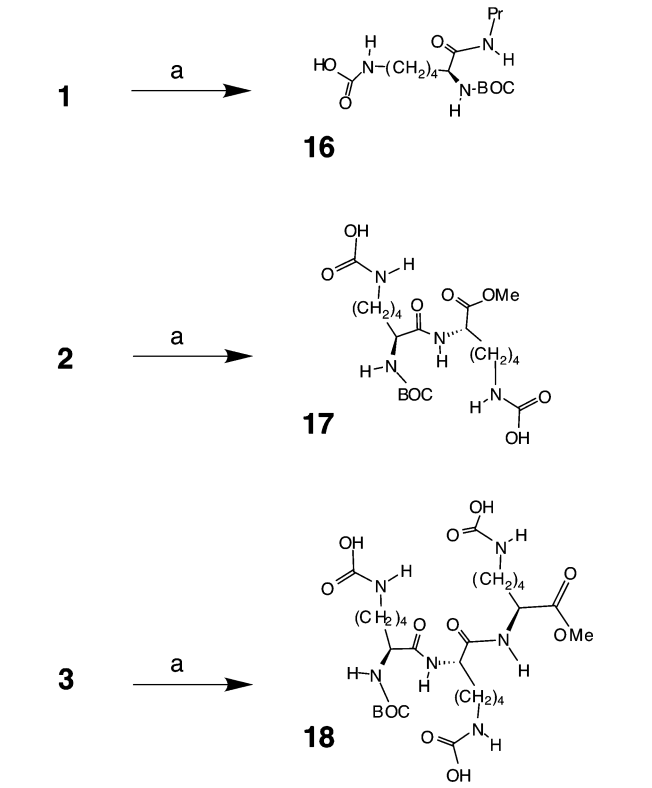
The presence of three reactive ϵ-NH_2 groups in lysine tripeptide **3** allowed for the preparation of cross-linked supramolecular polymer **6**. Bubbling CO_2 directly into the DMSO-d_6 solution of **3** resulted in the corresponding carbamic acid **18** (Scheme 2), which was characterized by NMR spectroscopy (see Figure 9B). At the same time, it was not possible to dissolve

SCHEME 1. Syntheses of Short (*L*)-Lysine Peptides[a]



[a] Conditions: (a) *n*-PrNH$_2$, EDCI·HCl, HOBt, *N*-methylmorpholine, CH_2Cl_2, 85%. (b) H_2, 10% Pd/C, MeOH, >95%. (c) **7**, EDCI·HCl, HOBt, *N*-methylmorpholine, CH_2Cl_2, 85%. (d) H_2, 10% Pd/C, MeOH, >95%. (e) AcCl, MeOH, 0 °C, 91%. (f) **7**, EDCI·HCl, HOBt, *N*-methylmorpholine, CH_2Cl_2, 82%. (g) H_2, 10% Pd/C, MeOH, >95%. (h) MeOH, 1 M aq NaOH, then 1 M aq HCl, 88%. (i) NH$_2$-(CH$_2$)$_{12}$-NH$_2$, EDCI·HCl, HOBt, *N*-methylmorpholine, CH_2Cl_2, 90%. (j) H_2, 10% Pd/C, MeOH, >95%.

SCHEME 2. Synthesis of (*L*)-Lysine-Based Carbamic Acids 16−18[a]



[a] Conditions: (a) CO_2, DMSO.

tripeptide **3** in $CHCl_3$ or any other aprotic solvents (hexane, benzene, toluene, MeCN, EtOAc, and THF), even at low

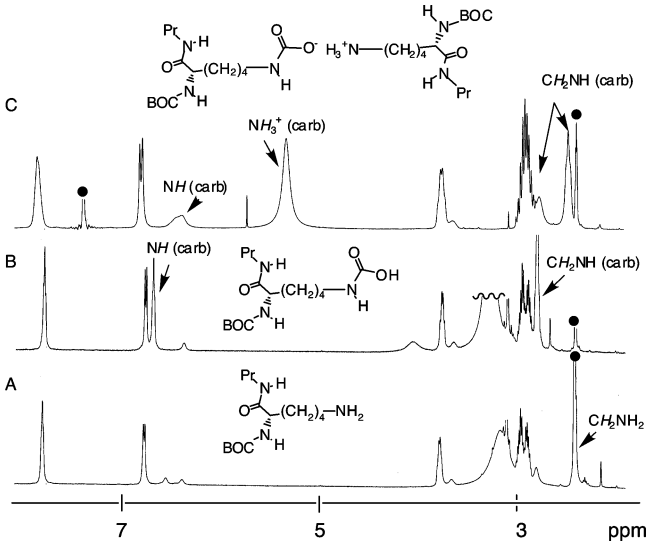


FIGURE 4. Portions of the ^{1}H NMR spectra (500 MHz, 295 ± 1 K, DMSO-d_6) of: (A) Boc-(*L*)-Lys-NHPr (**1**); (B) carbamic acid (**16**), prepared from **1** and CO_2; (C) carbamate **4**. Here and further in the paper, the residual solvent signals are marked as "•"and all spectral assignments were done by using 1D (^{1}H, ^{13}C, ^{13}C-DEPT 135) and 2D (^{1}H−^{1}H COSY, ^{13}C−^{1}H HETCOR, ^{1}H−^{13}C HMBC) NMR measurements in combination.

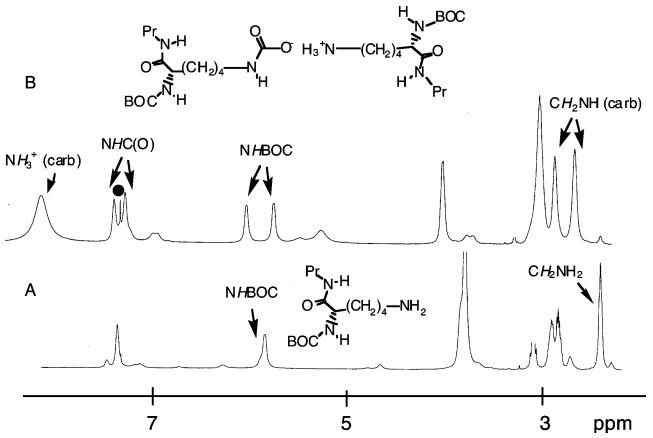


FIGURE 5. Portions of the ^{1}H NMR spectra (500 MHz, 295 ± 1 K, $CDCl_3$) of: (A) Boc-(*L*)-Lys-NHPr (**1**); (B) carbamate **4**, prepared from **1** and CO_2 in $CDCl_3$ **4**.

concentrations (0.02 M). The introduction of a longer alkyl chain into the structure of **3** also did not help. On the other hand, compound **3** was found to be well soluble in MeOH and also in its mixtures with $CHCl_3$ and benzene. Bubbling CO_2 through the clear solution of tripeptide **3** in benzene−MeOH (10:1) at ≥0.16 M concentrations successfully resulted in the formation of cross-linked polymer **6** as a colorless gel, which turned to a white powder when exposed to the air. Two new broad signals belonging to the carbamate N*H* and ammonium NH_3^+ protons appeared at 6.11 and 5.51 ppm, respectively (Figure 9C). The NH_3^+ signal showed significant concentration dependence. It was observed at 5.51 ppm for 0.16 M and appeared at 6.49 ppm when the concentration was increased to 0.64 M. On the other hand, the corresponding carbamate N*H* signal moved only slightly upfield from 6.11 to 5.94 ppm in the same concentration range. Characteristic broad peaks of α-CH_2 methylene protons were found at 2.85 and 2.57 ppm and did not show any concentration dependence (Figure 9C). Finally, the experiment

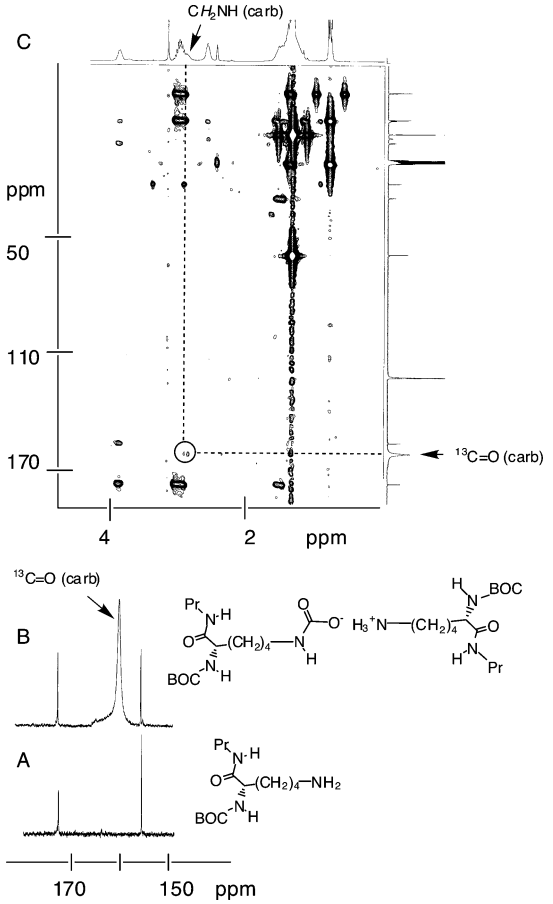


FIGURE 6. (A) Downfield portion of the ^{13}C NMR spectrum of compound **1** (75 MHz, 295 ± 1 K, $CDCl_3$). (B) Downfield portion of the ^{13}C NMR spectrum of carbamate **4** prepared with $^{13}CO_2$ (75 MHz, 295 ± 1 K, DMSO-d_6). (C) $^1H-^{13}C$ HMBC spectrum of carbamate **4** prepared from **1** in benzene−MeOH (10:1) by using $^{13}CO_2$ (75 MHz, 295 ± 1 K, DMSO-d_6).

with ^{13}C-labeled CO_2 gave evidence of the carbamate carbonyl group. A strong signal was found at 161.7 ppm, which is very similar to the chemical shifts for carbamates **4** and **5** (Figure 10).

Similarly, bubbling CO_2 through the clear solution of bridged lysine dipeptide **15** in benzene−MeOH (10:1) led to the formation of a colorless gel **19** (Figure 11). This cross-linked supramolecular polymer **19** was characterized by NMR techniques (see Supporting Information). Both carbamate materials **6** and **19** are stable when stored refrigerated as solids for at least several days. The reversibility of carbamate bonds in both compounds was proven by heating the samples in DMSO-d_6 in an NMR tube to ∼100 °C with simultaneous flashing with N_2 for several minutes. The ^1H NMR spectra obtained after this treatment were identical with those of starting amines **3** and **15**, respectively.

Preliminary Guest Entrapment Experiments. A number of cross-linked supramolecular polymers are known;[1] however, to our knowledge, they have not been used for guest storage and release purposes.[13] Cross-linked structures **6** and **19** possess multiple voids, which are generated between the peptide chains and the lysine−carbamate bridges. According to our calculations, these voids are of 20−25 Å dimensions, which makes them suitable for the entrapment of various organic substrates. We found that when CO_2 cross-links tripeptide **3** in the presence of an organic guest of 1−1.5 nm size, gel **6** instantly entraps it. In the preliminary experiment, we used gel **6** to trap a commercial fluorescent dye, such as coumarin 2, and employed conventional UV−vis spectrophotometry to monitor this process.

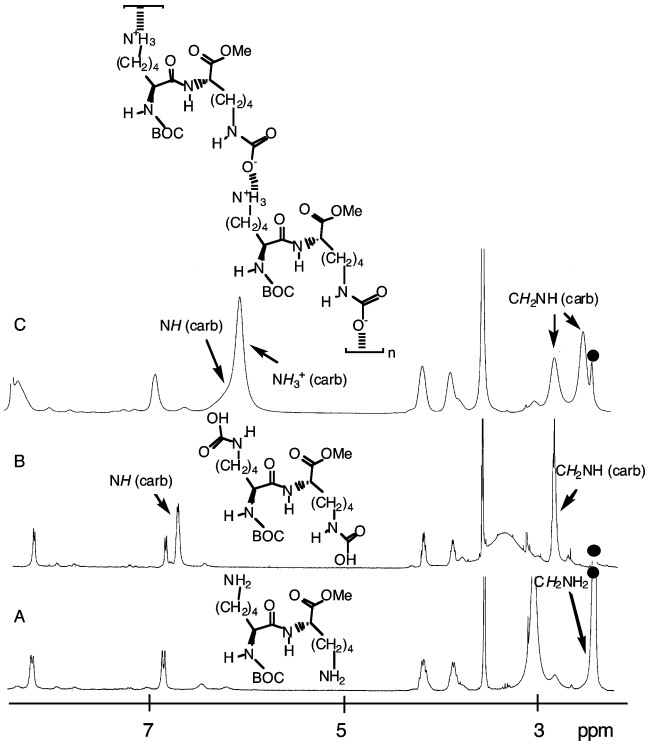


FIGURE 7. Portions of the ^1H NMR spectra (300 MHz, 295 ± 1 K, DMSO-d_6) of: (A) Boc-(*L*)-Lys-(*L*)-Lys-OMe (**2**); (B) carbamic acid **17**; (C) polymeric carbamate **5**, prepared from **1** and CO_2 in $CHCl_3$, followed by evaporation.

In a typical experiment, tripeptide **3** was dissolved in a small volume of benzene−MeOH (10:1) and then coumarin 2 was added in at a 2.5:1 molar ratio. CO_2 was bubbled through the solution for 10 min, and the decrease in the absorption of coumarin 2 in the supernatant solution was systematically recorded at $\lambda_{max} = 358$ nm (Figure 12). In this process, gel **6** was formed, which trapped the dye. As a consequence, the concentration of coumarin 2, and therefore its absorption, in solution decreased. From the absorbance measurements, up to ∼65 ± 3% of coumarin 2 was entrapped.[14] We feel that the same rules apply for other guests of comparable dimensions.

Conclusions

An approach has been proposed and demonstrated to construct supramolecular 2D and 3D polymeric structures from amino acids and short peptides upon their reaction with CO_2 gas. Short lysine-based peptides reversibly react with CO_2 to form polymeric gels. These are stable under laboratory conditions but release CO_2 at elevated temperatures and dissociate back to monomers. Accordingly, their architecture and properties are thermally switchable. These gels may also trap, store, and release

(13) For the preliminary results from this laboratory, see: Xu, H.; Rudkevich, D. M. *Org. Lett.* **2005**, *7*, 3223−3226.

(14) In the control experiment, CO_2 was bubbled through the solution of neat coumarin 2 and the absorption at $\lambda_{max} = 358$ nm was recorded. No visible changes were observed after 10 min.

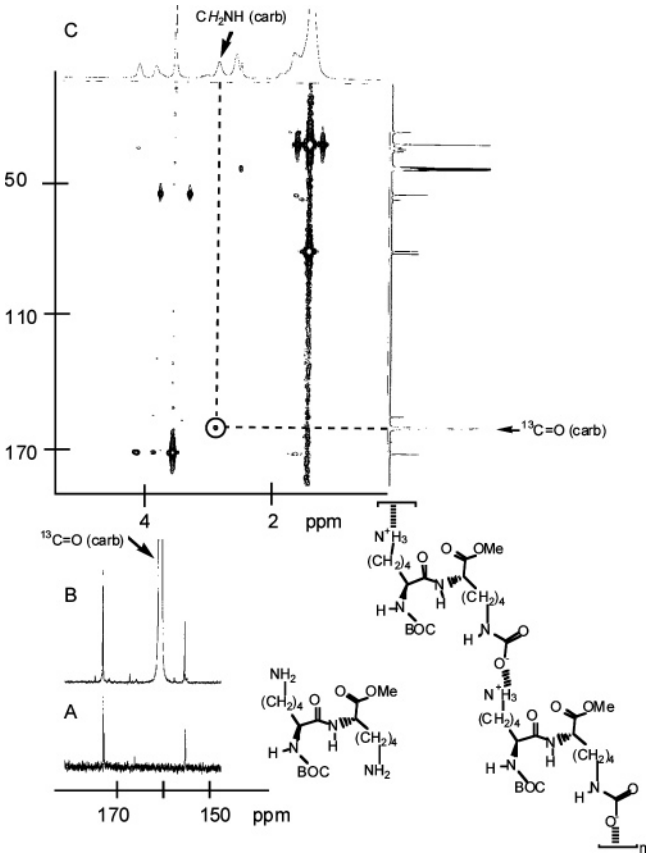


FIGURE 8. (A) Downfield portion of the ^{13}C NMR spectrum of compound **2** (75 MHz, 295 ± 1 K, DMSO-d_6). (B) Downfield portion of the ^{13}C NMR spectrum of carbamate **5** prepared with $^{13}CO_2$ (75 MHz, 295 ± 1 K, DMSO-d_6). (C) $^1H-^{13}C$ HMBC spectrum of carbamate **5** prepared from **2** in $CHCl_3$ by using $^{13}CO_2$ followed by evaporation (300 MHz, 295 ± 1 K, DMSO-d_6).

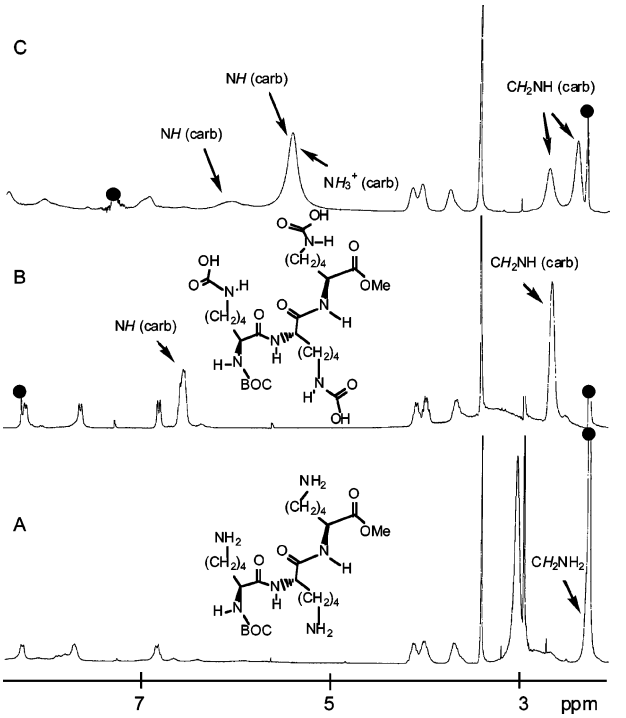


FIGURE 9. Portions of the ^1H NMR spectra (300 MHz, 295 ± 1 K, DMSO-d_6) of: (A) Boc-(*L*)-Lys-(*L*)-Lys-(*L*)-Lys-OMe (**3**); (B) carbamic acid **18**; (C) polymeric carbamate **6**, prepared from **3** and CO_2 in benzene−MeOH (10:1).

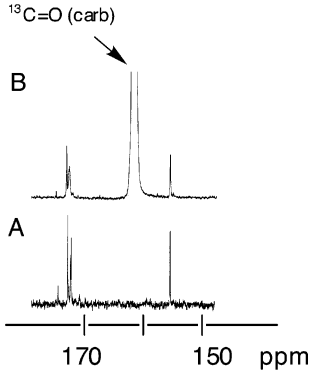


FIGURE 10. Downfield portion of the ^{13}C NMR spectra (75 MHz, 295 ± 1 K, DMSO-d_6) of: (A) tripeptide **3**; (B) carbamate **6** prepared from **3** and $^{13}CO_2$ in benzene−MeOH (10:1).

foreign molecules of industrial or biological interest. Such encapsulation studies are currently in progress. It would also be interesting to functionalize the monomeric peptides with molecular recognition sites, catalytic units, polymerizable groups, etc. and compose functional materials upon introduction of CO_2. This work has been started. Another important achievement is that CO_2 gas can be used as a building block. Considering the huge significance of CO_2 in the environment, our results offer means for creating environmentally-responsive materials.[15]

Experimental Section

General. Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 295 ± 1 °C on JEOL 300 and 500 MHz spectrometers. ^1H NMR spectra were recorded at 300 and 500 MHz. ^{13}C NMR spectra were recorded at 75 and 125 MHz. Chemical shifts were measured relative to residual nondeuterated solvent resonances. FTIR spectra were recorded using KBr pellets. Electrospray ionization (ESI) time-of-flight (TOF) reflectron experiments were performed at the Scripps Center for Mass Spectrometry. Samples were electrosprayed into the TOF reflectron analyzer at an ESI voltage of 4000 V and a flow rate of 200 μL/min. When applicable, the presence of solvent in analytical samples was confirmed by NMR spectroscopy. All experiments with moisture- and/or air-sensitive compounds were run under a dried N_2 atmosphere. For column chromatography, silica gel ((60 Å, 200−425 mesh) was used. Dipeptide **2** was obtained according to the known protocol.[16] Boc-Lys(Cbz)-OH (**7**) and (*L*)-Lys(Cbz)-OMe·HCl (**9**) were purchased from a commercial supplier. ^{13}C-labeled CO_2, containing 99 atom % ^{13}C and 3 atom % ^{18}O, was purchased commercially. Molecular modeling was performed using commercially available MacroModel 7.1.[9]

Boc-(*L*)-Lys(Cbz)-NH-*n*-Pr (8). Boc-Lys(Cbz)-OH (**7**; 500 mg, 1.31 mmol) was dissolved in CH_2Cl_2 (5 mL), and the solution was cooled in an ice bath to 0 °C. HOBt (209 mg, 1.31 mmol), EDCI·HCl (277 mg, 1.45 mmol), and *N*-methylmorpholine (0.304 mL, 2.76 mmol) were then added. The mixture was stirred for 15 min, after which *n*-propylamine (0.108 mL, 1.31 mmol) was added. The reaction mixture was stirred at 0 °C for 1 h and then at rt for the

(15) Xiaoding, X.; Moulijn, J. A. *Energy Fuels* **1996**, *10*, 305−325.

(16) Xu, H.; Kinsel, G. R.; Zhang, J.; Li, M.; Rudkevich, D. M. *Tetrahedron* **2003**, *59*, 5837−5848.

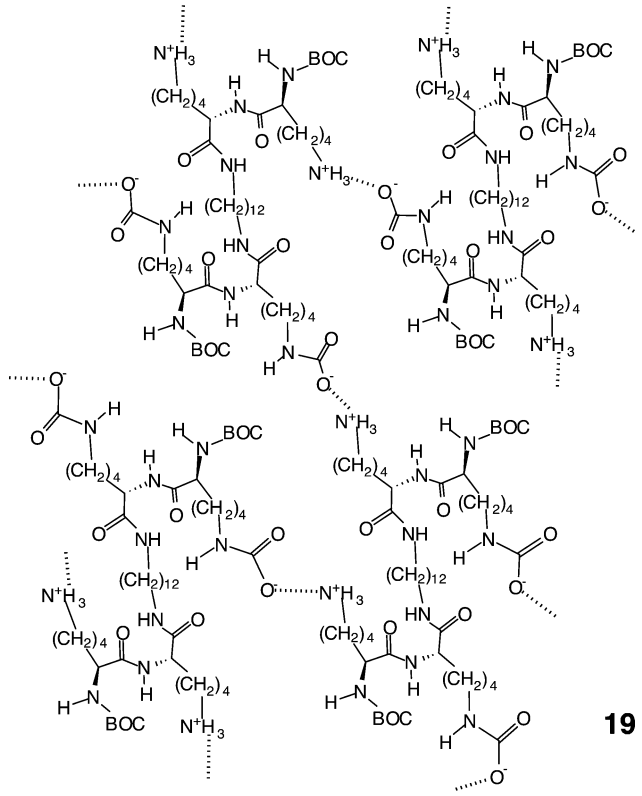


FIGURE 11. Cross-linked polymer **19** prepared from peptide-based tetramine **15** and CO_2.

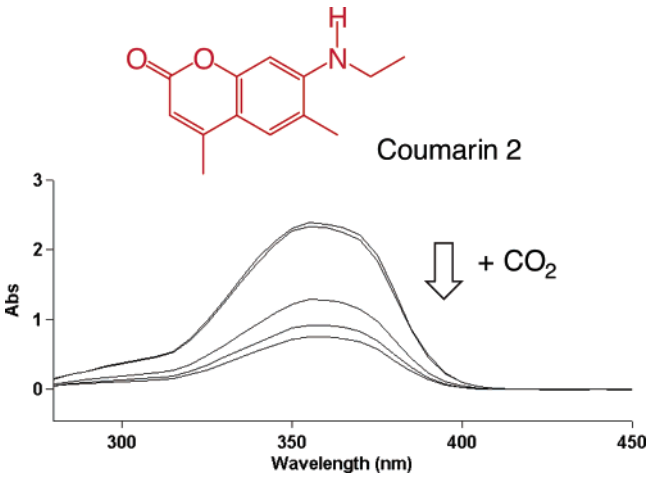


FIGURE 12. Guest entrapment experiment with tripeptide **3**, CO_2, and coumarin 2 in benzene−MeOH (10:1).

next 20 h. It was then diluted with CH_2Cl_2 (30 mL), and the organic layer was washed with H_2O (100 mL), 1 M aqueous solution of citric acid (100 mL), 10% (w/w) aqueous solution of $NaHCO_3$ (100 mL), and again with H_2O (100 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. Product **8** was obtained as a slightly yellow crystalline compound: yield 471 mg (85%); mp 91−92 °C. ^{1}H NMR (DMSO-d_6) δ 7.71 (t, J = 6.2 Hz, 1 H), 7.31 (m, 5 H), 7.20 (t, J = 5.5 Hz, 1 H), 6.70 (d, J = 8.3 Hz, 1 H), 4.97 (s, 2 H), 3.80−3.75 (m, 1 H), 3.05−2.85 (m, 4 H), 1.50−1.40, 1.40−1.35, and 1.25−1.15 (3 × m, 8 H), 1.34 (s, 9 H), 0.80 (t, J = 8.6 Hz, 3 H). ^{13}C NMR (DMSO-d_6) δ 172.5, 156.7, 155.8, 137.9, 128.9, 128.3, 78.4, 65.7, 54.9, 32.4, 29.7, 28.7, 23.4, 22.9, 11.8. IR (cm^{-1}, KBr) ν 3326, 2937, 2864, 1689, 1655, 1542, 1271, 1174. Anal. Calcd for $C_{22}H_{35}N_3O_5$: C, 62.69; H, 8.37; N, 9.97. Found: C, 62.40; H, 8.42; N, 10.13.

Boc-(*L*)-Lys-NHPr (1). Compound **8** (408 mg, 0.97 mmol) was dissolved in MeOH (5 mL) and added to the flask with Pd/C (10%, 30 mg) under N_2. The mixture was stirred under H_2 atmosphere for 16 h. The reaction mixture was then filtered through diatomaceous earth and evaporated under reduced pressure. The residue was then dried under high vacuum at rt to give derivative **1** as a colorless viscous oil that was used without further purification: yield 288 mg (>95%). ^{1}H NMR (DMSO-d_6) δ 7.74 (br, 1 H), 6.74 (d, J = 8.3 Hz, 1 H), 3.85−3.75 (m, 1 H), 3.05−2.95 (m, 2 H), 1.55−1.50, 1.50−1.45, 1.25−1.20 (3 × m, 8 H), 1.32 (s, 9 H), 0.82 (t, J = 7.8 Hz, 3 H). ^{13}C NMR (DMSO-d_6) δ 172.6, 155.9, 73.4, 54.3, 41.0, 40.8, 32.4, 31.4, 28.2, 22.7, 22.5, 11.2. Calcd for $C_{14}H_{29}N_3O_3$·0.4MeOH: C, 57.61; H, 10.27; N, 14.00. Found: C, 57.40; H, 10.00; N, 14.18.

Boc-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-OMe (10). This compound was prepared by a modification of the known procedure.[8] (*L*)-Lys(Cbz)-OMe·HCl (**9**; 500 mg, 1.51 mmol) and Boc-(*L*)-Lys(Cbz)-OH (**7**; 575 mg, 1.51 mmol) were dissolved in CH_2Cl_2 (30 mL), after which *N*-methylmorpholine (0.2 mL, 3.32 mmol) was added. The mixture was cooled to 0 °C in an ice bath, and then HOBt (224.5 mg, 1.661 mmol) was added. EDCI·HCl (318.4 mg, 1.661 mmol) and *N*-methylmorpholine (0.2 mL, 3.32 mmol) in CH_2Cl_2 (30 mL) were then added, and the reaction mixture was stirred for 1 h at 0 °C and then at rt overnight. The reaction mixture was then washed successively with H_2O (100 mL), 10% (w/w) aqueous solution of $NaHCO_3$ (100 mL), 10% (w/w) aqueous solution of citric acid (100 mL), and again with H_2O (100 mL). The organic layer was dried over $MgSO_4$ and then evaporated under reduced pressure to give **10** as a colorless viscous compound. The spectral and analytical data were in agreement with the previously published data.[8]

(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-OMe·HCl (11). Acetyl chloride (0.22 mL, 3.12 mmol) was added into MeOH (5 mL), and the mixture was stirred at 0 °C in an ice bath for 30 min. Boc-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-OMe (**10**; 196 mg, 0.132 mmol) in MeOH (5 mL) was then added, and the reaction mixture was stirred at rt overnight. After 16 h, no starting material was present in the reaction mixture according to TLC (SiO_2, CH_2Cl_2−MeOH, 96:4). The solvent was evaporated under reduced pressure, and then the residue was dissolved in MeOH (1 mL), after which diethyl ether (20 mL) was added. Product **11** was obtained as a white precipitate that was removed by filtration and dried under high vacuum: yield 168 mg (91%); mp 122−124 °C. ^{1}H NMR (DMSO-d_6) δ 8.80 (d, J = 6.9 Hz, 1 H), 8.16 (br, 3 H), 7.36−7.32 (m, 10 H), 7.28 (t, J = 6.4 Hz, 1 H), 7.22 (t, J = 5.5 Hz, 1 H), 5.00 (s, 4 H), 4.27−4.25 (m, 1 H), 3.80−3.78 (m, 1 H), 3.62 (s, 3 H), 3.00−2.98 (m, 4 H), 1.72−1.71 (m, 2 H), 1.64−1.59 (m, 2 H), 1.42−1.32 (m, 8 H). ^{13}C NMR (DMSO-d_6) δ 172.5, 169.4, 156.7, 156.7, 137.8, 137.8, 128.9, 128.3, 128.3, 65.7, 52.7, 52.5, 31.3, 29.6, 29.5, 23.2, 21.8. IR (cm^{-1}, KBr) ν 3336, 2934, 1734, 1689, 1657, 1543, 1282, 1258. ESI-MS TOF *m*/*z*: 591.2576 ([M − H]$^-$ calcd for $C_{29}H_{40}N_4O_7Cl$, 591.2591).

Boc-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-OMe (12). (*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-OMe·HCl (**11**; 154 mg, 0.26 mmol) and Boc-Lys(Cbz)-OH (**7**; 99 mg, 0.26 mmol) were dissolved in CH_2Cl_2 (10 mL), after which *N*-methylmorpholine (0.03 mL, 0.29 mmol) was added. The mixture was cooled to 0 °C in an ice bath, and then HOBt (39 mg, 0.29 mmol) was added, followed by the solution of EDCI·HCl (55 mg, 0.29 mmol) and *N*-methylmorpholine (0.03 mL, 0.29 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 1 h at 0 °C and then overnight at rt. The reaction mixture was then washed successively with H_2O (50 mL), 10% (w/w) aqueous solution of $NaHCO_3$ (50 mL), 1 M aqueous solution of citric acid (50 mL), and again with H_2O (50 mL). The organic layer was dried over $MgSO_4$ and then evaporated under reduced pressure to give **12** as a white crystalline compound: yield 196 mg (82%); mp 102−104 °C. ^{1}H NMR (DMSO-d_6) δ 8.23 (d, J = 6.5 Hz, 1 H), 7.68 (d, J = 8.3 Hz, 1 H), 7.40−7.30 (m, 15 H), 7.18 (t, J = 6.2 Hz, 3 H), 6.84 (d, J = 7.9 Hz, 1 H), 4.96 (s, 6 H), 4.30−4.25 (m, 1 H),

4.20−4.10 (m, 1 H), 3.90−3.80 (m, 1 H), 3.56 (s, 3 H), 3.00−2.90 (m, 6 H), 1.70−1.55, 1.50−1.40, and 1.30−1.20 (3 × m, 18 H), 1.33 (s, 9 H). ^{13}C NMR (DMSO-d_6) δ 172.9, 172.5, 172.3, 156.6, 155.9, 137.9, 128.9, 128.3, 78.7, 65.7, 55.0, 52.5, 52.3, 31.0, 29.7, 29.7, 29.5, 28.7, 23.3, 23.2. IR (cm^{-1}, KBr) ν 3325, 2939, 1693, 1640, 1539, 1255. ESI-MS TOF *m*/*z*: 919.4810 ([M + H]$^+$ calcd for $C_{48}H_{67}N_6O_{12}$, 919.4811). Anal. Calcd for $C_{48}H_{66}N_6O_{12}$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.28; H, 7.29; N, 9.35.

Boc-(*L*)-Lys-(*L*)-Lys-(*L*)-Lys-OMe (3). Pd/C (10%) (50 mg) was placed into a flask under N_2, after which Boc-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-OMe (**12**; 490 mg, 0.53 mmol) in MeOH (10 mL) was added. The mixture was stirred under H_2 atmosphere for 3 h, filtered through diatomaceous earth, and evaporated under reduced pressure. The residue was dried under high vacuum at rt to yield tripeptide **3** as a white crystalline compound: yield 265 mg (>95%); mp 226−228 °C (decomp). ^{1}H NMR (DMSO-d_6) δ 8.28 (br, 2 H), 7.73 (br, 2 H), 6.91 (br, 1 H), 4.30 (br, 1 H), 4.19 (br, 1 H), 3.90 (br, 1 H), 3.60 (s, 3 H), 1.65−1.50, 1.50−1.40, and 1.30−1.20 (3 × m, 18 H), 1.38 (s, 9 H). ^{13}C NMR (DMSO-d_6) δ 172.9, 172.5, 172.4, 155.9, 78.6, 54.8, 52.5, 52.4, 32.3, 31.9, 30.8, 29.5, 28.7, 23.0. ESI-MS TOF *m*/*z*: 517.3703 ([M + H]$^+$ calcd for $C_{24}H_{49}N_6O_6$, 517.3708).

Boc-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-OH (13). Boc-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-OMe (**10**; 690 mg, 1.05 mmol) was dissolved in MeOH (10 mL), and 1 M aqueous NaOH solution (1.6 mL) was then added. The mixture was stirred at rt for 2 h, the solvent was removed under reduced pressure, the residue was dissolved in H_2O (15 mL), and the pH was adjusted to 2−3 by slow addition of 1 M aqueous HCl. The resulting suspension was then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure to give product **13** as a colorless crystalline compound: yield 595 mg (88%); mp 50−55 °C. ^{1}H NMR (DMSO-d_6) δ 7.89 (d, J = 8.3 Hz, 1 H), 7.40−7.35 (m, 10 H), 7.19 (t, J = 5.9 Hz, 2 H), 6.78 (d, J = 8.9 Hz, 1 H), 4.97 (s, 4 H), 4.15−4.10 (m, 1 H), 3.90−3.80 (m, 1 H), 2.95−2.90 (m, 4 H), 1.70−1.65, 1.60−1.50, and 1.30−1.25 (3 × m, 12 H), 1.33 (s, 9 H). ^{13}C NMR (DMSO-d_6) δ 174.1, 172.8, 156.6, 155.8, 137.8, 128.9, 128.2, 78.5, 65.7, 54.5, 52.1, 32.2, 31.2, 29.7, 29.5, 28.7, 23.3, 23.1. IR (cm^{-1}, KBr) ν 3327, 2939, 1702, 1533, 1252. Anal. Calcd for $C_{33}H_{46}N_4O_9$: C, 61.67; H, 7.21; N, 8.72. Found: C, 61.25; H, 7.03; N, 8.66.

[Boc-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-NH(CH$_2$)$_6$-]$_2$ (14). Boc-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-OH (**13**; 400 mg, 0.622 mmol) and 1,12-diaminododecane (62 mg, 0.311 mmol) were dissolved in CH_2Cl_2 (10 mL), the mixture was cooled to 0 °C in an ice bath, and then HOBt (92 mg, 0.684 mmol) was added. A solution containing EDCI·HCl (131 mg, 0.684 mmol) and *N*-methylmorpholine (0.1 mL, 0.809 mmol) in CH_2Cl_2 (10 mL) was subsequently added, and the mixture was stirred at 0 °C for 1 h and at rt overnight. The reaction mixture was washed successively with H_2O (100 mL), 10% (w/w) aqueous solution of $NaHCO_3$ (100 mL), 1 M aqueous solution of citric acid (110 mL), and again with H_2O (100 mL). The organic layer was dried over $MgSO_4$ and then evaporated under reduced pressure to give **14** as a colorless crystalline compound: yield 405 mg (90%); mp 138−140 °C. ^{1}H NMR (DMSO-d_6) δ 7.97 and 7.66 (2 × d, J = 8.3 and 7.6 Hz, 2 H), 7.81 (t, J = 4.8 Hz, 2 H), 7.35−7.25 (m, 20 H), 7.20−7.15 (m, 4 H), 6.99 and 6.89 (2 × d, J = 6.5 and 8.3 Hz, 2 H), 4.96 (s, 8 H), 4.20−4.05 (m, 2 H), 3.85−3.75 (m, 2 H), 3.05−2.90 (m, 12 H), 1.55−1.40 (m, 20 H), 1.34 (br, 24 H), 1.18 (s, 18 H). ^{13}C NMR (DMSO-d_6) δ 172.4, 171.7, 156.6, 156.0, 137.9, 128.9, 128.3, 78.8, 78.7, 65.7, 55.1, 52.9, 39.0, 32.6, 31.9, 29.6, 29.3, 28.7, 26.9, 23.3, 23.0. IR (cm^{-1}, KBr) ν 3319, 2931, 1693, 1643, 1540, 1259. ESI-MS TOF *m*/*z*: 1449.8636 ([M + H]$^+$ calcd for $C_{78}H_{117}N_{10}O_{16}$, 1449.8643), 1471.8463 ([M + Na]$^+$ calcd for $C_{78}H_{116}N_{10}O_{16}Na$, 1471.8443). Anal. Calcd for $C_{78}H_{116}N_{10}O_{16}$·1.5$H_2O$: C, 63.43; H, 8.12; N, 9.48. Found: C, 63.17; H, 7.81; N, 9.33.

[Boc-(*L*)-Lys-(*L*)-Lys-NH(CH$_2$)$_6$-]$_2$ (15). Pd/C (10%) (50 mg) was placed into a flask flushed with N_2, and then [Boc-(*L*)-Lys-(Cbz)-(*L*)-Lys(Cbz)-(*L*)-Lys(Cbz)-NH(CH$_2$)$_6$-]$_2$ (**14**; 283 mg, 0.195 mmol) in MeOH (10 mL) was added. The mixture was stirred under H_2 atmosphere overnight, filtered through diatomaceous earth, and evaporated under reduced pressure. The residue was then dried under high vacuum at rt to give tetraamine **15** as a colorless crystalline compound: yield 178 mg (>95%); mp 62−64 °C. ^{1}H NMR (DMSO-d_6) δ 7.92 and 7.82 (2 × br, 4 H), 7.02 (br, 2 H), 4.18 (br, 2 H), 3.85 (br, 2 H), 3.04, 2.98, and 2.87 (3 × br, 4 H), 2.55 (br, 8 H), 1.57, 1.49, and 1.37 (3 × br, 44 H), 1.22 (s, 18 H). ^{13}C NMR (DMSO-d_6) δ 172.4, 171.8, 156.2, 155.9, 78.7, 78.6, 55.1, 52.9, 39.8, 38.9, 32.6, 32.0, 31.5, 29.5, 29.2, 28.7, 26.8, 23.2, 22.9. ESI-MS TOF *m*/*z*: 913.7165 ([M + H]$^+$ calcd for $C_{46}H_{93}N_{10}O_8$, 913.7172), 935.6986 ([M + Na]$^+$ calcd for $C_{46}H_{92}N_{10}O_8Na$, 935.6991).

General Procedure for the Preparation of Carbamic Acids (16−18). Dry CO_2 was bubbled through the solution of Boc-(*L*)-Lys-NHPr (**1**; 0.5 mmol) in DMSO-d_6 (0.5 mL) in the NMR tube for 10 min, after which the NMR spectra were recorded. The solution remained clear during this time. **16:** ^{1}H NMR (DMSO-d_6) δ 7.72 (t, J = 5.5 Hz, 1 H), 6.73 (d, J = 9.6 Hz, 1 H), 6.65 (t, J = 5.5 Hz, 1 H), 3.85−3.80 (m, 1 H), 3.05−2.90 (m, 2 H), 2.90−2.85 (m, 2 H), 1.55−1.50, 1.50−1.40, and 1.25−1.15 (3 × m, 8 H), 1.34 (s, 9 H), 0.82 (t, J = 7.8, 3 H). ^{13}C NMR (DMSO-d_6) δ 172.5, 157.5, 155.6, 78.3, 54.8, 32.3, 29.9, 28.6, 23.5, 22.8, 11.9. Dry CO_2 gas was bubbled through the solution of Boc-(*L*)-Lys-(*L*)-Lys-OMe (**2**; 39 mg, 0.1 mmol) in DMSO-d_6 (0.5 mL) in the NMR tube for 10 min. **17:** ^{1}H NMR (DMSO-d_6) δ 8.09 (d, J = 7.3 Hz, 1 H), 6.78 (d, J = 8.3, 1 H), 6.70−6.65 (m, 2 H), 4.20−4.15 (m, 1 H), 3.90−3.85 (m, 1 H), 3.61 (s, 3 H), 2.90−2.85 (m, 4 H), 1.65−1.55, 1.55−1.40, and 1.30−1.15 (3 × m, 12 H), 1.36 (s, 9 H). ^{13}C NMR (DMSO-d_6) δ 173.0, 157.6, 155.8, 78.6, 54.6, 52.3, 32.1, 31.2, 29.9, 29.8, 28.7, 23.1, 22.8. **18:** ^{1}H NMR (DMSO-d_6) δ 8.25 (d, J = 6.9 Hz, 1 H), 7.68 (d, J = 7.9 Hz, 1 H), 6.87 (d, J = 7.9 Hz, 1 H), 6.70−6.60 (m, 3 H), 4.30−4.20 and 4.20−4.10 (2 × m, 2 H), 3.85−3.80 (m, 1 H), 3.58 (s, 3 H), 2.90−2.80 (m, 6 H), 1.65−1.40 and 1.30−1.15 (2 × m, 18 H), 1.34 (s, 9 H). ^{13}C NMR (DMSO-d_6) δ 173.0, 172.5, 172.3, 157.6, 155.9, 78.6, 55.4, 54.9, 52.5, 52.3, 32.6, 32.1, 31.0, 29.9, 29.8, 29.7, 28.7, 23.4, 23.1, 22.8. **Carbamic acid from 15:** ^{1}H NMR (DMSO-d_6) δ 8.02, 7.83, and 7.69 (3 × br, 4 H), 7.03 and 6.94 (2 × br, 2 H), 6.67 (br, 3 H), 4.20−4.15 and 4.10−4.05 (2 × m, 2 H), 3.83 (br, 2 H), 3.05−3.00 (m, 4 H), 2.88 (br, 6 H), 1.60−1.45 and 1.40−1.30 (2 × m, 44 H), 1.22 (s, 18 H). ^{13}C NMR (DMSO-d_6) δ 172.5, 171.7, 157.7, 156.0, 78.7, 55.1, 52.8, 39.0, 32.7, 32.0, 29.9, 29.5, 29.3, 28.6, 26.8, 23.4, 23.0.

Carbamate (4). Method A. Dry CO_2 was bubbled through the solution of Boc-(*L*)-Lys-NHPr (**1**; 140 mg, 0.49 mmol) in $CDCl_3$ (0.5 mL) in the NMR tube for 5 min, after which the spectra were recorded. The solution remained clear during this time. ^{1}H NMR ($CDCl_3$) δ 8.05 (br, 3 H), 7.32 and 7.21 (2 × br, 2 H), 6.00 (br, 1 H), 5.73 (br, 1 H), 5.27 (br, 1 H), 4.10−3.95 (m, 2 H), 3.20−3.00 (m, 4 H), 2.94 (br, 2 H), 2.74 (br, 2 H), 1.70−1.60, 1.55−1.50, and 1.50−1.40 (3 × m, 16 H), 1.34 (s, 18 H), 0.82 (t, J = 6.9 Hz, 6 H). ^{13}C NMR ($CDCl_3$) δ 172.6, 172.4, 163.2, 156.1, 79.6, 54.5, 54.3, 41.4, 41.1, 39.2, 32.8, 32.2, 32.1, 28.4, 23.1, 22.8, 22.6, 11.4. **Method B.** Dry CO_2 was bubbled through the solution of **1** (140 mg, 0.49 mmol) in $CHCl_3$ (1 mL) for 10 min. The solution remained clear during this time. The solvent was evaporated under reduced pressure at rt, and the viscous residue was dried at rt under high vacuum for 5 h to give material **4** as a white crystalline powder. Calcd for $C_{29}H_{58}N_6O_3$·2$CHCl_3$: C, 43.42; H, 7.05; N, 9.80. Found: C, 43.67; H, 7.30; N, 9.61. **Method C.** Dry CO_2 was bubbled through the solution of **1** (158 mg, 0.57 mmol) in a mixture of benzene (1 mL) and MeOH (0.1 mL) for 40 min. The solution remained clear during this time. The residual solvent was evaporated under reduced pressure at rt, and the colorless viscous residue was dried at rt under high vacuum for 5 h to give carbamate **4** as a white crystalline powder. ^{1}H NMR (DMSO-d_6) δ 7.79 (br, 2 H), 6.76 (d, J = 8.9 Hz, 2 H), 6.35 (br, 1 H), 5.33 (br, 4 H), 3.85−

3.75 (m, 2 H), 3.05−2.85 (m, 5 H), 2.55 (br t, 2 H), 1.6−1.1 (br m, 16 H), 1.32 (s, 18 H), 0.78 (t, J = 8.9 Hz, 6 H). ^{13}C NMR (DMSO-d_6) δ 172.5, 158.2, 155.8, 78.4, 54.9, 32.3, 32.4, 29.9, 28.7, 23.3, 22.9, 11.8.

Carbamate (5). Dry CO_2 was bubbled through the solution of Boc-(*L*)-Lys-(*L*)-Lys-OMe (**2**; 200 mg, 0.515 mmol) in $CHCl_3$ (1 mL) for 10 min. During this period, material **5** was formed as a colorless gel. This was removed, washed quickly with $CHCl_3$ (2 mL), and dried under high vacuum at rt for 20 min. ^{1}H NMR (DMSO-d_6) δ 8.25−8.15 (m, 1 H), 6.85 (d, J = 7.2 Hz, 1 H), 6.23 (br, 1 H), 5.11 (br, 6 H), 4.17 (br, 1 H), 3.89 (br, 1 H), 3.57 (s, 3 H), 2.86 (br, 2 H), 2.56 (br, 2 H), 1.65−1.50 (m, 12 H), 1.34 (s, 9 H). ^{13}C NMR (DMSO-d_6) δ 173.0, 160.3, 155.8, 78.5, 54.5, 52.3, 51.8, 40.6, 40.4, 32.1, 31.7, 31.0, 30.2, 28.7, 22.9. Calcd for $C_{19}H_{36}N_4O_7 \cdot 0.4CHCl_3$: C, 48.52; H, 7.64; N, 11.67. Found: C, 48.51; H, 7.68; N, 12.08.

Carbamate (6). Dry CO_2 was bubbled through the solution of Boc-(*L*)-Lys-(*L*)-Lys-(*L*)-Lys-OMe (**3**; 41 mg, 0.079 mmol) in a mixture of benzene (0.5 mL) and MeOH (0.05 mL) for 5 min. The solution turned turbid, and a colorless gel was formed. This was removed and washed quickly with benzene (1 mL). The gel quickly turned to a white solid when exposed to the air. It was dried under high vacuum at rt for 1 h to yield polymeric material **6**. ^{1}H NMR (DMSO-d_6) δ 8.40 (br, 1 H), 8.04 (br, 1 H), 6.94 (br, 1 H), 6.11 (br, 1 H), 5.51 (br, 6 H), 4.25 (br, 1 H), 4.15 (br, 1 H), 3.87 (br, 1 H), 3.57 (s, 3 H), 2.85 (br, 2 H), 2.57 (br, 2 H), 1.65−150 and 1.40−1.25 (2 × m, 18 H), 1.33 (s, 9 H). ^{13}C NMR (DMSO-d_6) δ 173.0, 172.6, 172.4, 161.7, 155.8, 78.4, 54.9, 52.6, 52.3, 32.3, 32.1, 30.8, 30.2, 28.7, 23.0.

Carbamate (19). Dry CO_2 was bubbled through the solution of [Boc-(*L*)-Lys-(*L*)-Lys-NH$(CH_2)_6$-]$_2$ (**15**; 60 mg, 0.066 mmol) in a mixture of benzene (0.5 mL) and MeOH (0.05 mL) for 10 min. The solution turned turbid, and a colorless gel was formed. This was removed and washed quickly with benzene (1 mL). The gel turned to a white solid powder when exposed to the air. It was dried under high vacuum at rt for 1 h to give material **19**. ^{1}H NMR (DMSO-d_6) δ 7.95 and 7.79 (2 × br, 4 H), 7.06 (br, 2 H), 6.3−5.3 (br, 11 H), 4.17 and 4.07 (2 × br, 2 H), 3.86 (br, 2 H), 3.05−2.98 (br m, 8 H), 2.61 (br, 4 H), 1.35−1.2 (br m, 44 H), 1.21 (s, 18 H). ^{13}C NMR (DMSO-d_6) δ 172.5, 171.8, 160.5, 156.0, 78.6, 55.2, 52.9, 39.0, 32.5, 31.9, 30.3, 29.5, 29.3, 28.7, 26.8, 23.1.

Entrapment Experiments. In a typical procedure, CO_2 was gently bubbled through the solution of tripeptide **3** (50 mg, 0.1 mmol) and coumarin 2 (8.4 mg, 0.04 mmol) in benzene−MeOH (10:1) (0.5 mL) over a period of 10 min. Aliquots of the supernatant solution (0.0025 mL) were taken before CO_2 bubbling and after 2, 5, 7, and 10 min of CO_2 bubbling and diluted to 1 mL with the same solvent. UV−vis spectra were recorded; the decrease in coumarin 2 absorption at λ_{max} = 358 nm was followed. A colorless gel was formed within 1−2 min of CO_2 bubbling. The experiments were performed at least in triplicate, giving a good reproducibility.

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Supporting Information Available: High-field ^{1}H and ^{13}C NMR spectra for compounds **1**−**19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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