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Reversible Chemistry of CO_2 in the Preparation of Fluorescent Supramolecular Polymers

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The chemistry between CO_2 and primary amines was used to construct novel types of supramolecular polymers and networks. Fluorescent self-assembling gel **2** was prepared, which employs both hydrogen bonding and dynamic, thermally reversible carbamate bonds. As precursors, biscalixarenes **1**, **3**, **4**, **6**, and **7** were synthesized, which strongly aggregate ($K_D \geq 10^6$ M^{-1} per capsule) in apolar solution with the formation of linear self-assembling polymers. Polymer $\mathbf{1}_n$ possesses CO_2-philic primary amino groups on the periphery. CO_2 rapidly reacts with chains $\mathbf{1}_n$ in apolar solvents and cross-links them with the formation of multiple carbamate salt bridges. Three-dimensional polymeric network **2** was characterized by ^{13}C NMR spectroscopy and SEM. Addition of competitive solvent breaks hydrogen bonding in **2** but does not influence the carbamate linkers. Carbamate salt **9** was obtained. On the other hand, thermal release of CO_2 from **2** and **9** was easily accomplished (1 h, 100 °C) with retaining the hydrogen-bonding capsules. Thus, three-dimensional polymeric networks **2** were transformed back to linear polymeric chains $\mathbf{1}_n$ without their breakup. Multiple pyrene fluorophores, attached on the periphery of **2**, cause strong fluorescence of the gel with benzene. When ~5% nitrobenzene was gelated together with benzene, fluorescence strongly decreases due to the energy transfer from the pyrene donors in gel **2** to trapped nitrobenzene molecules. This opens a way to switchable fluorescent materials.

Introduction

Supramolecular polymers are a novel class of macromolecules in which monomeric units are kept together by reversible, noncovalent forces.[1] These mainly include hydrogen bonds and metal−ligand (Lewis acid−base) interactions. Supramolecular polymers thus combine spectacular properties of self-assembly with conventional polymeric features. As a consequence, structural parameters and architecture of supramolecular polymers can be switched "on−off" through the main chain assembly dissociation. We recently introduced a strategy to build *two-parameter* switchable supramolecular polymers/networks which utilize hydrogen bonding *and* dynamic chemistry between CO_2 and primary amines (e.g., carbamate chemistry) (Figure 1).[2] We employed CO_2 as a cross-linking agent. Linear, hydrogen-bonding polymeric chains were reversibly converted into robust three-dimensional networks by simply introducing and thermally releasing CO_2. In this paper, we address *functionalization* of such supramolecular polymers and networks. We now report on the preparation of switchable supramolecular materials with fluorescent properties.

The chemistry between CO_2 and amines has been known for years. It leads to robust carbamate salts.[3,4] The reaction, however, is thermally reversible, and CO_2 can be released back by simply heating at ≥80 °C. This property has been utilized in amine-based, reusable polymeric "CO_2 scrubbers",[5] some ionic liquids,[6] in the preparation of organogels[7] and imprinting polymers.[8] Our approach is sketched in Figure 2.

Monomeric units **1** were designed, which (a) strongly aggregate in apolar solution with the formation of

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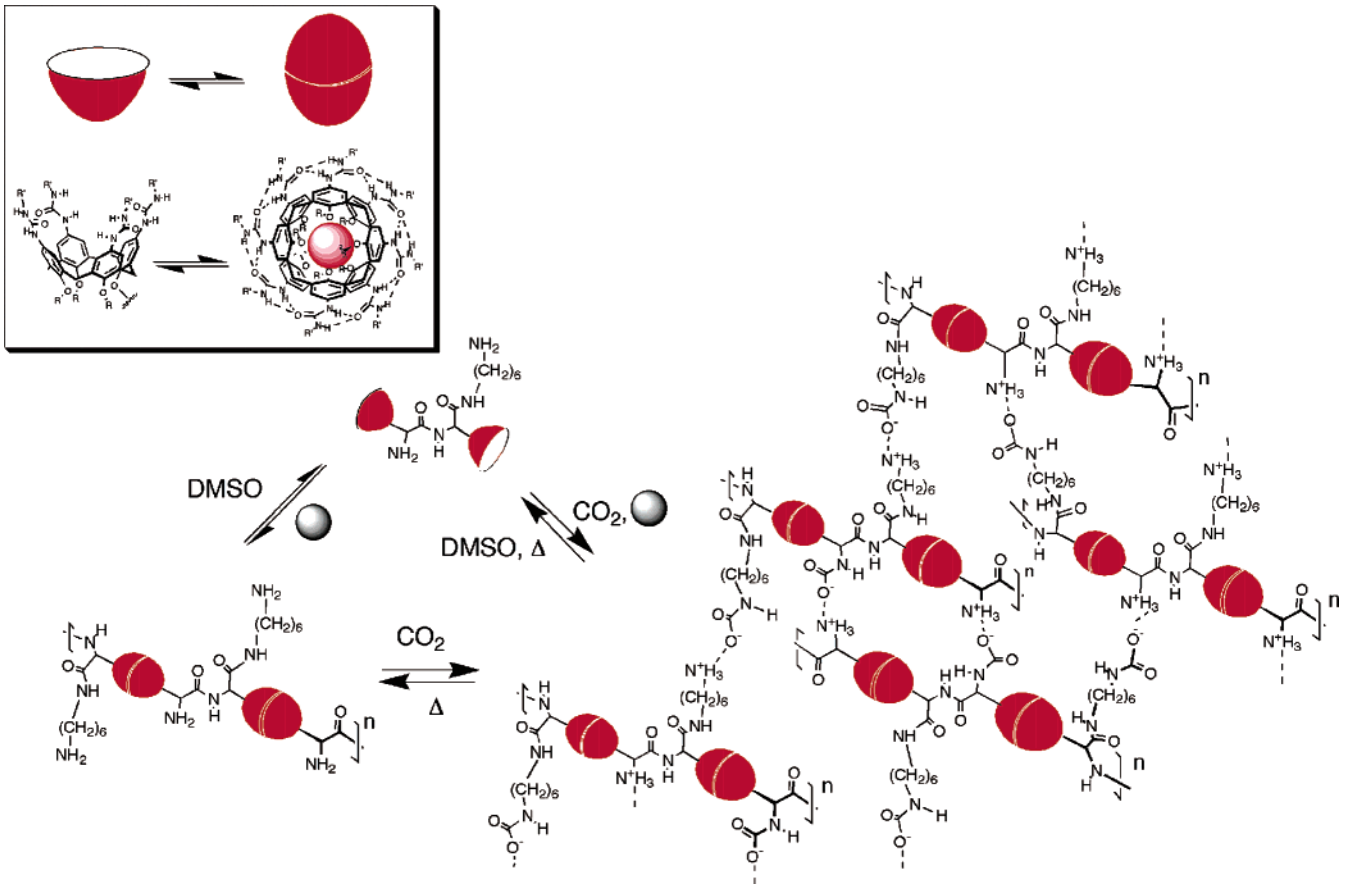

FIGURE 1. CO_2 reversibly cross-links polymeric calixarene chains into a three-dimensional supramolecular network.

polymeric, hydrogen bonding capsules $\mathbf{1}_n$, (b) possess a "CO_2-philic" primary amino group on the periphery, and (c) were functionalized with a fluorophore. The CO_2-philic amino groups were introduced roughly perpendicular to the main self-assembling chain $\mathbf{1}_n$. In apolar solvent, once CO_2 is added, multiple carbamate bridges form and result in three-dimensional supramolecular networks with multiple fluorophores. Addition of competitive solvent breaks self-assembly but not the carbamate linkers. Thermal release of CO_2 can be easily accomplished, but it does not influence the noncovalent aggregates, and the capsules do not dissociate.

Results and Discussion

Design. For this project, we took advantage of calix[4]arene tetraureas as well-known self-assembling modules. Discovered 10 years ago by Rebek[9] and Böhmer,[10] these form well-defined dimeric capsules in apolar solution ($K_D \geq 10^6$ M^{-1}), which are held together by a seam of 16 intermolecular C═O···H−N hydrogen bonds at the upper rims. This results in a rigid cavity of ~200 Å^3, which reversibly encapsulates a solvent molecule or a benzene-sized guest. When two calix[4]arene tetraureas are covalently linked at their lower rims, hydrogen bonding yields supramolecular polymeric capsules.[11]

In structure **1**, two calixarene tetraurea modules are linked with a di-*l*-lysine chain. The calixarenes were attached to the ϵ-NH_2 ends, so the dipeptide orients them away from each other, in roughly opposite directions.[12] According to molecular modeling, this prevents the intramolecular assembly. Such design affords supramolecular polymeric chains with the degree of polymerization (further, DP) of ~3×10^2 at NMR concentrations.[2] Accordingly, upon self-assembly molecules **1** form long chains $\mathbf{1}_n$ with CO_2-philic multiple hexamethyleneamines attached to the carboxylic side of each dipeptide, and the pyrene fragments appended to the α-NH_2 groups.

Synthesis. Our synthetic strategy is based on modular combination of calixarene building blocks with amino acids and short peptides.[13] This allows for great flexibility in the construction of multifunctional nanostructures. Biscalixarene tetraurea **1** was prepared from calixarenes **3**−**7** (Scheme 1).

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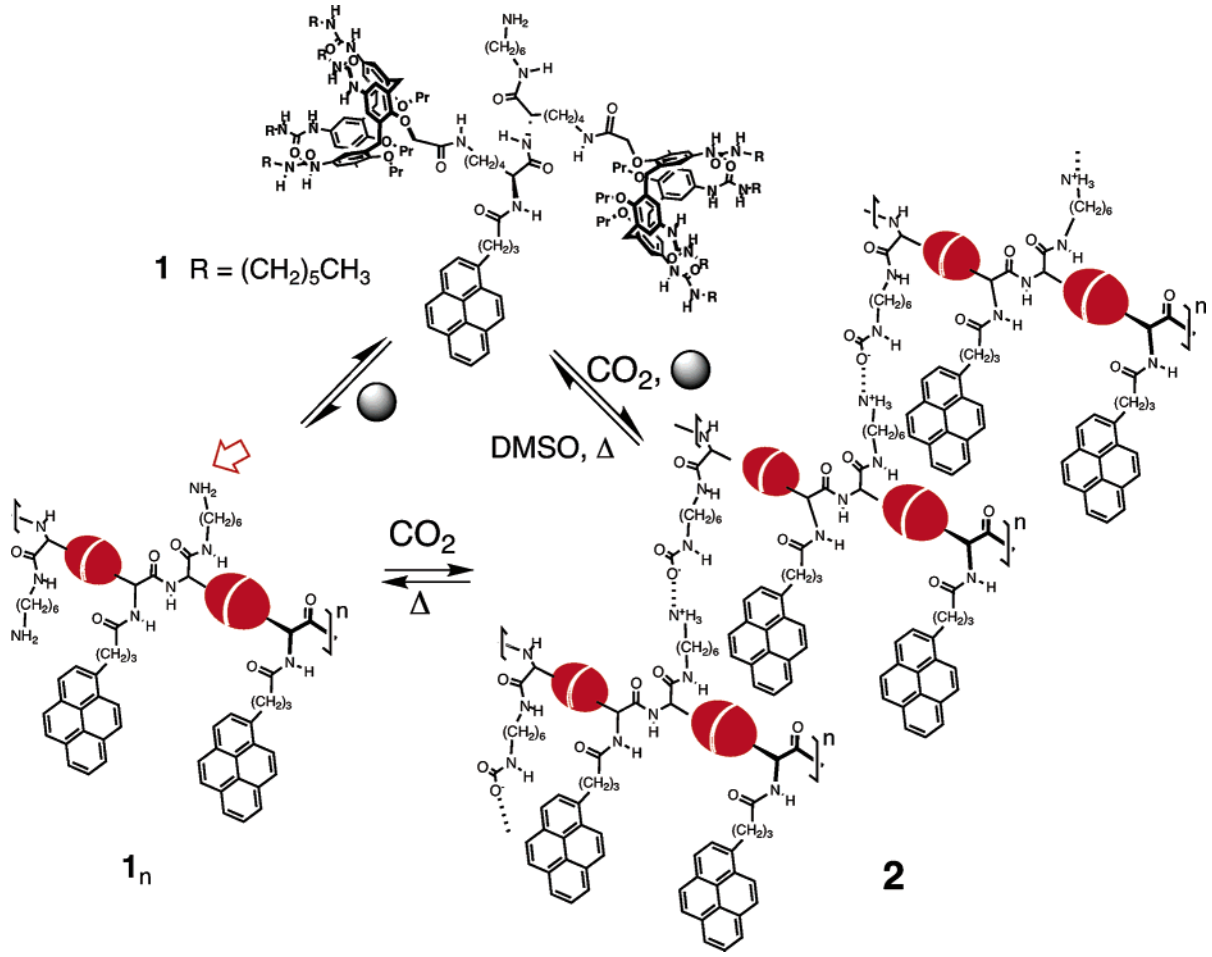

FIGURE 2. Fluorescent, carbamate cross-linked supramolecular network.

In short, biscalixarene dipeptide **3** was synthesized from acid **5** and bis-*N*-BOC-protected dilysine, followed by quantitative deprotection of resulting **4**[2] with TFA in THF and subsequent washing with aq NaOH. 1-Pyrenebutyric acid was introduced through the EDCI coupling (Et_3N, DMAP, DMF) with the formation of derivative **6** in 79% yield. At the next step, the methyl ester was hydrolyzed with $Bu_4N^+OH^-$ (H_2O/THF, 94%), and BOC-NH-$(CH_2)_6$-NH_2 was then attached (EDCI, Et_3N, DMAP, DMF), resulting in biscalixarene **7** in 65% yield. The terminal BOC-protection was then quantitatively cleaved (TFA, CH_2Cl_2), and the amino group was liberated with aq NaOH for the subsequent reaction with CO_2.

Monomeric calixarene tetraurea **8**, functionalized with *N*-α-BOC-L-lysine methyl ester, was readily prepared from calixarene acid **5** for spectroscopic comparisons (DCC, HOBT, DMF, 70%).

Self-Assembly. We previously established a strong tendency for biscalixarene dipeptides, such as **4** and its structural relatives, to polymerize through hydrogen bonding (NMR spectroscopy, viscosity measurements, encapsulation studies, molecular modeling, etc.).[2,12] The double-logarithmic relationship between specific viscosity η_{sp} and concentration for biscalixarene **4**, with a slope of ~2, implies the formation of reversibly breakable polymers, the size of which increases with concentration.[2] Furthermore, addition of small quantities of calixarene **5** to the $CHCl_3$ solution of biscalixarene **4** resulted in a dramatic decrease in viscosity. Acting as a chain stopper, compound **5** competitively participates in hydrogen bonding with the calixarene fragments in **4** and its polymeric chains. From these measurements, the DP value of ~3 × 10^2 was calculated for **4** at 20 mM, which corresponds to the average molar mass of ~8 × 10^5 g/mol. Similar behavior is fully expected for structurally related biscalixarene **1**, which is only modified on the periphery. Theoretical estimations[14] are in good agreement with the experiment: with the dimerization constant $K_D \geq 10^6$ M^{-1} for each calixarene capsule in $\mathbf{1}_n$, the average DP of at least 10^2 is predicted at the NMR concentration range.

Aggregation of **1**, its immediate precursor **7**, and model calixarene tetraurea **8** was studied in detail by ^1H NMR spectroscopy. Calixarene **8** is only expected to dimerize, while biscalixarenes **1** and **7** should form polymeric chains. Nevertheless, the spectroscopic behavior of all three is similar. Due to the lack of symmetry in capsule **8**·**8**, a multiple set of NH urea signals was recorded in $CDCl_3$ and benzene-d_6 between 6 and 8.5 ppm (for example, Figure 3B). These are characteristically shifted downfield ($\Delta\delta \geq 2$), compared to model, nondimerized ureas, showing the key features[7−11] of the capsule formation. Indeed, statistically, both a proximal and a distal

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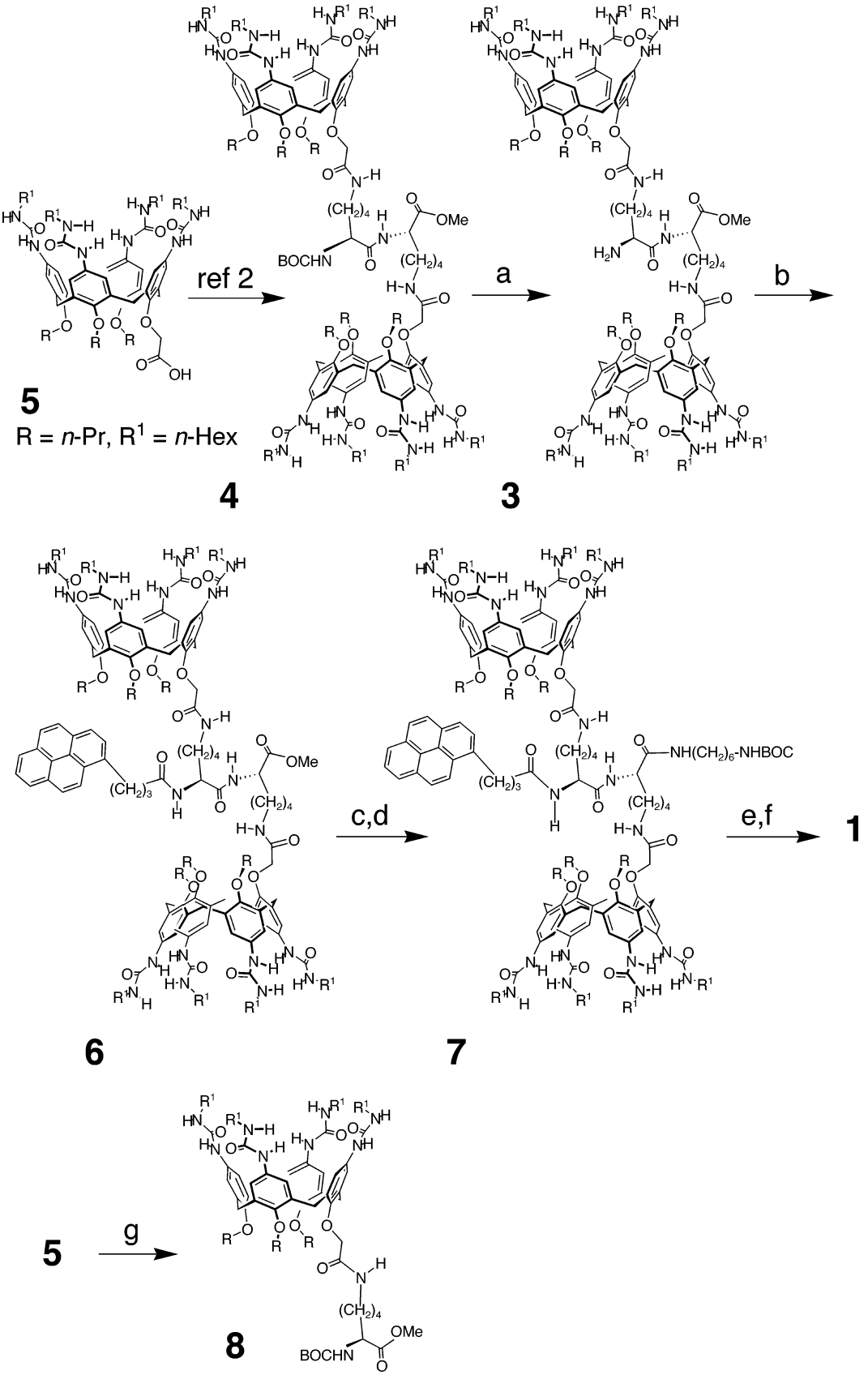
SCHEME 1[a]



[a] Key: (a) TFA, THF, then 10% aq NaOH, $CHCl_3$, 92%; (b) 1-pyrenebutyric acid, Et_3N, EDCI, DMAP, DMF, 79%; (c) $Bu_4N^+OH^-$, H_2O/THF, 94%; (d) BOCNH-$(CH_2)_6$-NH_2, EDCI, Et_3N, DMAP, DMF, 65%; (e) TFA, CH_2Cl_2; (f) 10% NaOH, $CHCl_3$, 92%; (g) *N*-α-Boc-L-lysine-OMe, DCC, HOBT, DMF, 70%.

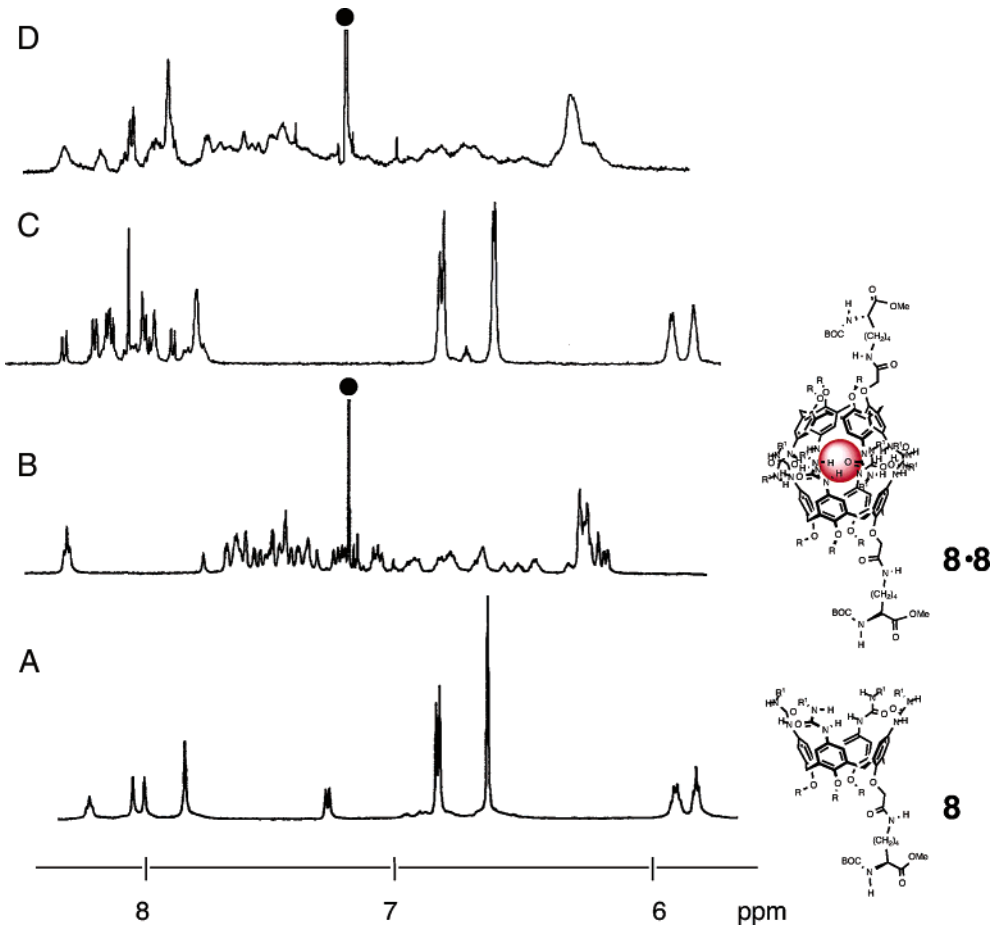


FIGURE 3. Downfield portions of ^{1}H NMR spectra (500 MHz, 295 ± 1 K) of: (A) calixarene **8** in DMSO-d_6; (B) capsule **8•8** in $CDCl_3$, only one regioisomer is depicted; (C) biscalixarene **7** in DMSO-d_6; (D) polymeric $\mathbf{7}_n$ in $CDCl_3$. Spectra of **1** and $\mathbf{1}_n$ are similar to those of **7** and $\mathbf{7}_n$, respectively. The residual solvent signals are marked with a ●.

regioisomers of **8·8** form, with respect to the orientation of the acetamide $OCH_2C(O)NH$ substituents at the lower rims of each calixarene **8**.[11] Moreover, the circular array of hydrogen bonds is arranged either clockwise or counterclockwise. Capsule **8·8** dissociates to monomeric tetraurea **8** in more competitive DMSO-d_6. This results in a much simpler ^{1}H NMR picture, reflecting the presence of an apparent vertical symmetry plane in **8** (Figure 3A). For example, three Ar*N*H*C*(O) urea singlets in a ratio of 1:1:2 at 8.03, 7.99, and 7.83 ppm and three aromatic C*H* singlets in a ratio 2:2:4 at 6.82, 6.81, and 6.61 ppm are clearly seen in the downfield part of the spectrum.

Analogously, biscalixarenes **1** and **7** exhibit quite simple and resolved spectra in DMSO-d_6 and complex and also broad spectra in $CDCl_3$. Such a difference implies supramolecular polymerization in apolar media. The chemical shifts for the upper rim urea NH signals in **1** and **7** are in the same region as for model **8** in both solvents (Figure 3).

The interiors of polymeric capsules $\mathbf{1}_n$ are, most probably, filled with solvent. The encapsulation behavior of $\mathbf{1}_n$ is of significant interest and will be explored in upcoming papers.

Reaction with CO_2. Bubbling the CO_2 gas through solutions of **1** (e.g., $\mathbf{1}_n$) in benzene or benzene−$CHCl_3$ yields material **2**, which is an insoluble gel (Figures 2 and 4). The main chains in **2** are held together by hydrogen bonding assembly of capsules, and multiple carbamate $-N^+H_3\cdots O^-C(O)NH-$ bridges cross-link these chains. The result is a three-dimensional network, since the side amine groups are oriented in all three dimensions.

Formation of the carbamate bridges was confirmed by ^{13}C NMR spectroscopy. Using $^{13}CO_2$ gas, we prepared the carbamate ^{13}C-labeled gel **2**. In the ^{13}C NMR spectrum of biscalixarene **1**, prior the reaction with the gas, in DMSO-d_6 five C=O carbonyl signals were clearly detected—four for the amide fragments at 172.9, 172.0, 171.6, and 169.3 ppm and one intense signal for the upper rim ureas at 155.8 ppm (Figure 5A). In the spectrum of the ^{13}C-labeled salt **9**, which is formed upon dissociation of the ^{13}C-labeled polymer **2** in DMSO-d_6, in addition to these signals, a new singlet of higher intensity appeared at 160.7 ppm (Figure 5B). This is attributed to the carbamate HN-^{13}C(O)O$^-$ group.[3] The signal disappeared after heating solution **9** for 1 h at ∼100 °C and bubbling N_2 through it.

Due to the low solubility in most apolar solvents, the corresponding ^{1}H NMR spectra of gel **2** are difficult to obtain. At the same time, **2** fully dissociates to carbamic salt **9** in polar DMSO-d_6 (Figure 4). Similar to derivatives **1**, **7**, and **8**, this results in a simpler ^{1}H NMR spectrum, reflecting the apparent vertical symmetry plane in the molecule.

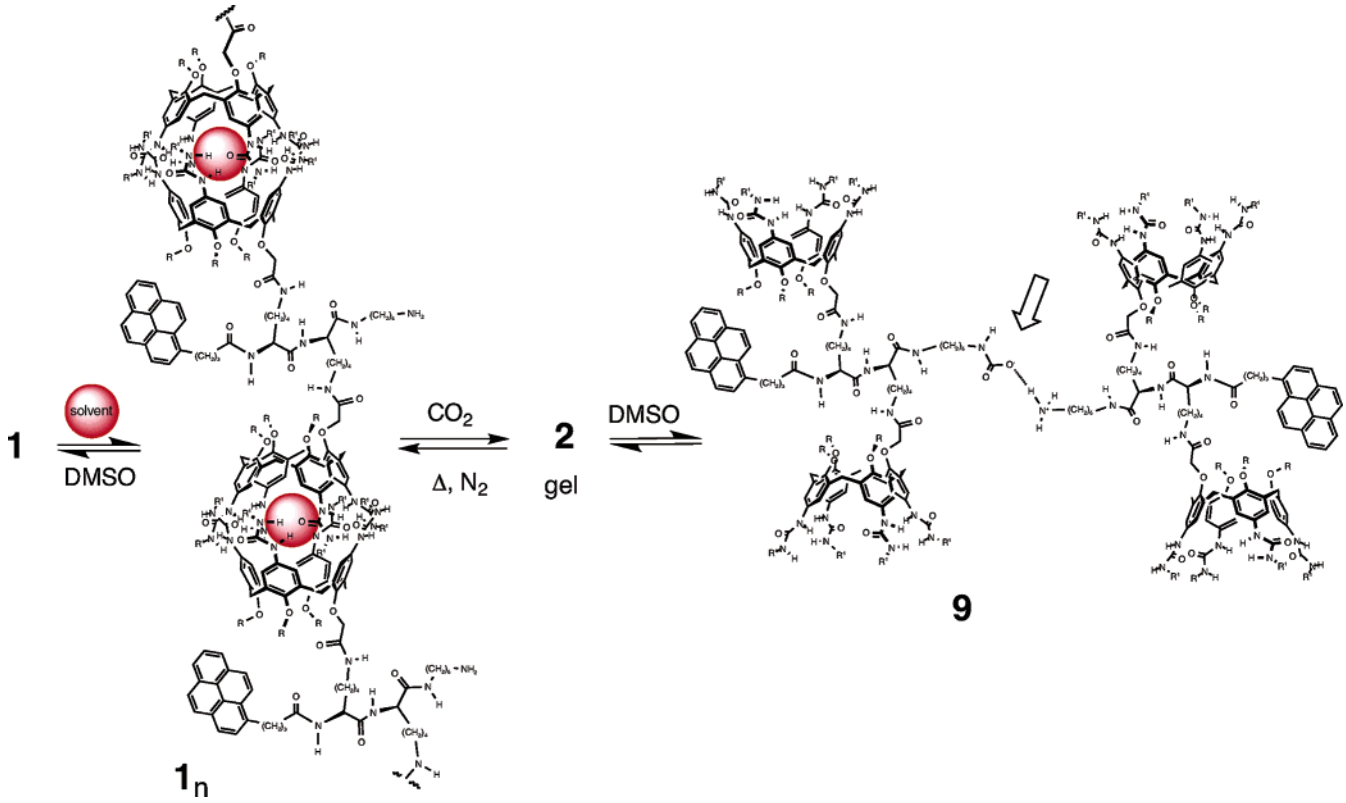


FIGURE 4. Reaction between biscalixarene **1** and CO_2. Formation of carbamate cross-linked supramolecular polymer **2** and its dissociation to carbamate **9**.

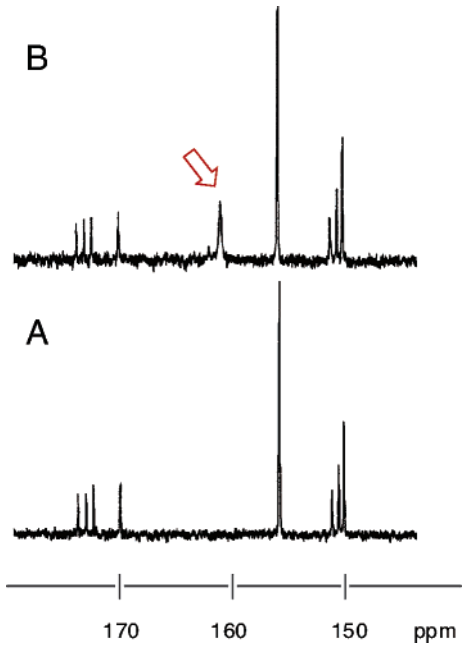


FIGURE 5. Downfield portions of ^{13}C NMR spectra (125 MHz, DMSO-d_6, 295 ± 1 K) of (A) biscalixarene **1**; (B) carbamate salt **9** obtained upon dissociation of ^{13}C-labeled gel **2**. The gel was prepared from **1** and $^{13}CO_2$ in benzene. The carbamate ^{13}C-enriched signal is marked.

Properties. Gel **2** assembles and dissipates in a two-fashion way—upon changing either the solvent polarity or temperature. The calixarene capsules completely dissociate in DMSO with the formation of carbamate salt **9** (Figure 4). It, most probably, undergoes further solvolysis, generating loose ion pairs. The carbamate C–N bonds are not broken under these conditions. At the same time, they can be destroyed upon heating for 1 h at ~100 °C, thus releasing CO_2. I In apolar solution, linear, hydrogen-bonded polymer $\mathbf{1}_n$ forms, and in DMSO biscalixarene **1** is completely regenerated. Gel **2** can be reconstructed simply by reintroducing CO_2.

Further insight into the aggregation mode and morphology in material **2** was obtained with scanning electron microscopy (SEM). For these freeze-dried samples, xerogels **2** were obtained from **1** and CO_2 in benzene and benzene–nitrobenzene, 95:5. The three-dimensional network in the xerogels is obvious (Figure 6). Of particular interest are well-defined pores of ~1–3 μm diameter, which can be used for guest/solvent entrapment.

Material **2** possesses multiple fluorophore units, brought together through hydrogen bonding and carbamate bridges, and thus may act as a vehicle for energy migration.[15] The aggregation degree and therefore the fluorophore local concentrations can be controlled and switched on–off, as described previously.

In the preliminary photophysical experiments, we noticed a striking contrast in fluorescent behavior of xerogels **2** obtained from benzene and benzene–nitrobenzene, 95:5 solutions (Figures 7 and 8). The former is strongly fluorescent (λ_{ex} = 347 nm), but the latter is not. Nitrobenzene is known to quench fluorescence of pyrene.[16]

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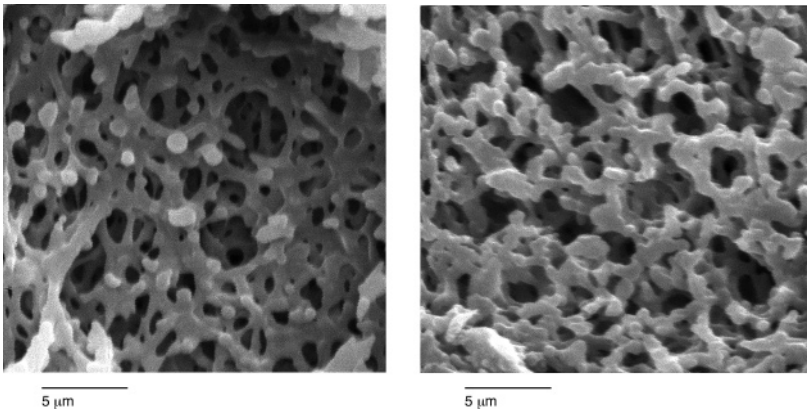

FIGURE 6. SEM pictures of xerogels **2** obtained upon bubbling CO_2 to benzene (left) and benzene−nitrobenzene 95:5 (right) solutions of **1** (bar 5 μm).

FIGURE 7. Xerogels **2** obtained upon bubbling CO_2 to benzene (left) and benzene−nitrobenzene 95:5 (right) solutions of **1**.

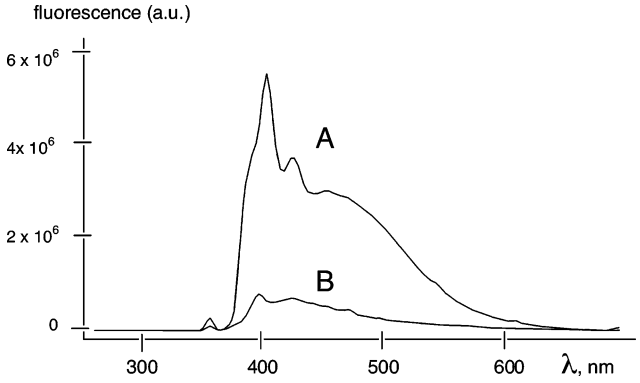

FIGURE 8. Fluorescence measurements with gels **2** obtained upon bubbling CO_2 to benzene (A) and benzene−nitrobenzene 95:5 (B) solutions of **1** (λ_{ex} = 347 nm).

Incorporated within the gel's pores, molecules of nitrobenzene appear in close proximity to the multiple pyrene donors, and the energy transfer effectively occurs. In another experiment, dropwise addition of nitrobenzene (up to 10% v/v) to the benzene suspension of fluorescent xerogel **2**, preliminary obtained from benzene, resulted in the fluorescence disappearance within seconds. These observations could be useful in the design of switchable light-harvesting materials.

Conclusions and Outlook

CO_2 extensively circulates in the environment through a number of processes known as the carbon cycle.[17] The development of novel methods of chemical fixation and utilization of this gas is of great interest,[18] and carbamate chemistry obviously may help. CO_2 can now be used to build switchable, supramolecular polymeric materials and gels. These can be further functionalized. We are currently testing the "on−off" photophysics of such gels. Characterization of their mechanical properties is in progress as well.[19] We are also exploring and incorporating other functionalities within the dynamic three-dimensional networks, such as capsules, ionophores, catalytic sites, polymerizable groups for covalent cross-linking, etc. Using the described approach and given highly diverse peptide syntheses, the capabilities to build multifunctional self-assembling materials are beyond the limits.

Experimental Section

General Methods. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively (295 ± 1 °C). Chemical shifts were measured relative to residual nondeuterated solvent resonances. FTIR spectra were recorded in KBr pellets. All experiments with moisture- and/or air-sensitive compounds were run under a dried nitrogen atmosphere. For column chromatography, silica gel 60 Å 200−425 mesh was used. Parent tetrahydroxycalix[4]-arene[20] and calixarene precursors **4**[2] and **5**[2,11] were prepared according to the published procedures.

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Biscalixarene Dipeptide (3). A solution of the BOC-protected dipeptide **4** (0.5 g, 0.18 mmol) in THF (15 mL) was treated with TFA (10 mL) and then stirred at rt for 4 h. The reaction mixture was concentrated in vacuo to afford pure TFA-salt of **3**: ^{1}H NMR (DMSO-d_6) δ 8.78 (d, J = 7.3 Hz, 1 H), 8.24 (br s, 2 H), 8.06 (s, 2 H), 8.01 (s, 2 H), 7.84 (s, 4 H), 6.80 (s, 4 H), 6.79 (s, 4 H), 6.62 (s, 4 H), 6.59 (s, 4 H), 5.9 (m, 4 H), 5.8 (m, 4 H), 4.40 (s, 4 H), 4.33 (d, J = 12.3 Hz, 4 H), 4.24 (d, J = 12.3 Hz, 4 H), 4.2 (m, 1 H), 3.8 (m, 1 H), 3.75 (t, J = 7.0 Hz, 8 H), 3.69 (t, J = 7.0 Hz, 4 H), 3.62 (s, 3 H), 3.2 (m, 4 H), 3.0 (m, 24 H), 1.9−1.1 (4 x m, 88 H), 0.85 (m, 42 H); FTIR ν 3347, 3082, 2932, 2860, 1670, 1599, 1474, 1205; ESI-MS m/z 2719 (M^+, calcd for $C_{149}H_{224}N_{20}O_{23}F_3$ 2719). The TFA-salt of **3** was then dissolved in $CHCl_3$ (60 mL) and washed with 10% NaOH (2 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to give free amine **3** as a colorless solid (0.44 g, 92%): ^{1}H NMR (DMSO-d_6) δ 8.19 (br s, 3 H), 8.04 (s, 2 H), 7.99 (s, 2 H), 7.83 (s, 4 H), 6.82 (s, 4 H), 6.81 (s, 4 H), 6.62 (s, 8 H), 5.86 (m, 4 H), 5.78 (t, J = 5.0 Hz, 4 H), 4.38 (s, 4 H), 4.34 (d, J = 12.3 Hz, 4 H), 4.25 (d, J = 12.3 Hz, 4 H), 3.76 (t, J = 7.0 Hz, 8 H), 3.71 (t, J = 7.0 Hz, 4 H), 3.62 (s, 3 H), 3.22 (m, 4 H), 3.0 (m, 24 H), 1.9−1.1 (4 x m, 88 H), 0.9 (m, 42 H); ^{13}C NMR (DMSO-d_6) δ 175.9, 173.1, 169.3, 155.7, 151.2, 150.7, 150.3, 135.3, 135.1, 134.9, 134.4, 134.1, 133.9, 118.7, 118.5, 79.6, 77.2, 76.5, 74.7, 54.9, 52.2, 52.0, 35.5, 31.6, 31.4, 30.3, 29.8, 26.6, 23.4, 22.8, 22.6, 14.4, 10.5; ESI-MS m/z 2608 ([M + H]$^+$, calcd for $C_{147}H_{224}N_{20}O_{21}$ 2607).

Biscalixarene (6). To a stirred and ice-cooled solution of the TFA-salt of **3** (0.5 g, 0.18 mmol) in DMF (15 mL) was added Et_3N (0.05 mL, 0.36 mmol), and then after 15 min, successively 1-pyrenebutyric acid (0.10 g, 0.36 mmol), EDCI (0.14 g, 0.72 mmol), and DMAP (cat.). The mixture was allowed to stir for 30 min at 0 °C and for 24 h at room temperature and then filtered, concentrated under reduced pressure, diluted with $CHCl_3$ (100 mL), and washed with water (3 × 100 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel eluting with $CHCl_3$−CH_3OH, 95:5 to afford pyrene functionalized calixarene **6** (0.41 g, 79%): mp > 180 °C de; ^{1}H NMR (DMSO-d_6) δ 8.4−7.9 (m, 17 H), 7.8 (m, 4 H), 6.8 (m, 8 H), 6.6 (m, 8 H), 5.9 (m, 4 H), 5.8 (m, 4 H). 4.4 (m, 2 H), 4.36 (s, 4 H), 4.32 (d, J = 12.8 Hz, 4 H), 4.20 (d, J = 12.8 Hz, 4 H), 3.70 (m, 12 H), 3.59 (s, 3 H), 3.30 (t, J = 7.3 Hz, 2 H), 3.21 (m, 4 H), 3.0 (m, 24 H), 2.31 (t, J = 6.9 Hz, 2 H), 2.0 (m, 2 H), 1.8−1.1 (4 × m, 88 H), 0.9 (m, 42 H); FTIR ν 3337, 2957, 2930, 2858, 1654, 1601, 1558, 1473, 1213.

Biscalixarene (7). To a stirred and ice-cooled solution of dipeptide **6** (0.3 g, 0.10 mmol) in THF/H_2O, 15:1 (10 mL) was added a 40% aqueous solution of n-Bu_4NOH (0.2 mL, 0.30 mmol). The mixture was allowed to stir for 1.5 h at 0 °C, after which H_2O (20 mL) was added, and the pH was adjusted to 2 with aq 1 M HCl. The product was extracted with $CHCl_3$ (2 × 30 mL), and the organic layer was dried over anhydrous Na_2SO_4 and then evaporated. The resulting free acid (0.27 g, 94%) was used without further purification: ^{1}H NMR (DMSO-d_6) δ 8.40−7.88 (m, 17 H), 7.83 (br s, 4 H), 6.82 (m, 8 H), 6.61 (br s, 8 H), 5.9 (m, 4 H), 5.8 (m, 4 H), 4.4 (m, 2 H), 4.34 (s, 4 H), 4.31 (d, J = 12.8 Hz, 4 H), 4.20 (d, J = 12.8 Hz, 4 H), 3.7 (m, 12 H), 3.30 (t, J = 7.3 Hz, 2 H), 3.2 (m, 4 H), 3.1−2.9 (m, 24 H), 2.97 (t, J = 6.9 Hz, 2 H), 2.0 (m, 2 H), 1.8−0.9 (4 × m, 88 H), 0.9 (m, 42 H); FTIR ν 3337, 2958, 2930, 2858, 1654, 1601, 1558, 1473, 1415, 1214. To a stirred and ice-cooled solution of the obtained acid (0.30 g, 0.10 mmol) in DMF (15 mL) were added *N*-BOC-1,6-diaminohexane (0.05 mL, 0.20 mmol), EDCI (0.08 g, 0.4 mmol), DMAP (catalyst), and Et_3N (0.03 mL, 0.2 mmol). The mixture was allowed to stir for 30 min at 0°C and for 24 h at rt, filtered, concentrated, diluted with $CHCl_3$, and washed with water (3 × 100 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel eluting with $CHCl_3$−CH_3OH, 96:4 to afford biscalixarene **7** (0.20 g, 65%): mp 160 °C dec; ^{1}H NMR (DMSO-d_6) δ 8.40−7.75 (m, 22 H), 6.82 (m, 8 H), 6.71 (t, J = 6.0 Hz, 1 H), 6.6 (m, 8 H), 5.9 (m, 4 H), 5.8 (m, 4 H), 4.35 (br s, 4 H), 4.28 (d, J = 12.8 Hz, 4 H), 4.20 (d, J = 12.8 Hz, 4 H), 3.7 (m, 12 H), 3.30 (t, J = 7.3 Hz, 2 H), 3.2 (m, 4 H), 3.1−2.9 (m, 26 H), 2.85 (dt, J = 6.9 Hz, J = 6.4 Hz, 2 H), 2.31 (t, J = 7.3 Hz, 2 H), 2.0 (m, 2 H), 1.33 (s, 9 H), 1.8−1.1 (5 x m, 96 H), 0.9 (m, 42 H); FTIR ν 3335, 2930, 2859, 1653, 1558, 1473, 1245, 1214; MALDI-TOF m/z 3083 ([M + Na]$^+$, calcd for $C_{177}H_{258}N_{22}O_{23}Na$ 3083). Anal. Calcd for $C_{177}H_{258}N_{22}O_{23}$: C, 69.43; H, 8.49; N, 10.06. Found: C, 69.08; H, 8.45; N, 9.85.

Biscalixarene (1). A solution of the BOC-protected calixarene **7** (0.2 g, 0.07 mmol) in CH_2Cl_2 (10 mL) was treated with TFA (10 mL) and then stirred at rt for 4 h. The reaction mixture was concentrated in vacuo to afford the pure TFA-salt. This was then dissolved in $CHCl_3$ (60 mL) and washed with 10% NaOH (2 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to give free amine **1** (0.19 g, 92%): ^{1}H NMR (DMSO-d_6) δ 8.3−7.7 (m, 22 H), 6.8 (m, 8 H), 6.6 (m, 8 H), 5.9 (m, 4 H), 5.8 (m, 4 H), 4.34 (br s, 4 H), 4.28 (d, J = 12.8 Hz, 4 H), 4.22 (d, J = 12.8 Hz, 4 H), 4.2 (m, 1 H), 4.1 (m, 1 H), 3.7 (m, 12 H), 3.30 (t, J = 7.3 Hz, 2 H), 3.2 (m, 4 H), 3.1−2.8 (m, 26 H), 2.55 (t, J = 6.9 Hz, 2 H), 2.31 (t, J = 7.8 Hz, 2 H), 2.0 (m, 2 H), 1.8−1.1 (5 x m, 96 H), 0.9 (m, 42 H); FTIR ν 3337, 2958, 2930, 2859, 1654, 1601, 1559, 1416, 1245, 1214; ESI-TOF m/z 2960.9355 ([M + H]$^+$, calcd for $C_{172}H_{250}N_{22}O_{21}$ 2960.9243). Anal. Calcd for $C_{172}H_{250}N_{22}O_{21}\cdot 2CHCl_3$: C, 65.27; H, 7.96; N, 9.62. Found: C, 64.93; H, 7.81; N, 9.32.

Reaction of Biscalixarene 1 with CO_2. Freshly prepared biscalixarene **1** (120 mg) was dissolved in benzene (5 mL), and dry CO_2 (or $^{13}CO_2$) was then bubbled through the solution for 2 min at ~35 °C. Material **2** was dried in high vacuum at rt for 6 h. Upon dissolution in DMSO, **2** dissociated to carbamate salts **9**: ^{1}H NMR (DMSO-d_6) δ 8.35 (br), 8.22 (m), 8.17 (m), 8.08 (m), 8.03 (m), 7.95−7.75 (m), 6.82 (m), 6.60 (m), 5.90 (m), 5.81 (m), 4.35 (m), 4.29 (m), 4.21 (m), 3.80−3.60 (m), 3.35 (m), 3.20 (m), 3.10−2.80 (m), 2.49 (m), 2.32 (m), 2.01 (m), 1.72 (m), 1.54 (m), 1.34 (m), 1.23 (m), 0.84 (m); ^{13}C NMR (DMSO-d_6) δ 172.9, 172.0, 171.6, 169.3, 160.7, 155.8, 151.3, 151.26, 150.7, 150.3, 137.1, 135.2, 135.1, 135.0, 134.4, 134.2, 134.0, 131.5, 131.0, 129.9, 128.9, 128.7, 128.0, 127.97, 127.7, 127.0, 126.6, 125.4, 125.3, 124.8, 124.75, 124.1, 118.8, 118.6, 118.5, 77.3, 76.5, 74.8, 53.6, 53.2, 41.9, 39.2, 39.0, 35.5, 32.9, 31.6, 30.4, 30.1, 29.5, 28.2, 26.7, 26.6, 23.7, 23.5, 23.0, 22.96, 22.9, 22.7, 14.5, 10.6.

***N*-a-BOC-*N*-e-(calix[4]arenetetraurea)-L-lysine, Methyl Ester (8).** To an ice-cooled solution of *N*-a-BOC-L-lysine methyl ester (0.26 g, 1.0 mmol) in DMF (30 mL) were added calixarene tetraurea acid **5** (1.19 g, 1.0 mmol), DCC (0.41 g, 2.0 mmol), and HOBt (0.27 g, 2.0 mmol). The mixture was allowed to stir for 30 min at 0°C and for 24 h at rt, filtered, concentrated, diluted with $CHCl_3$, and washed successively with 1 N $NaHSO_4$ (4 × 100 mL), water (3 × 100 mL), 1 N $NaHCO_3$(4 × 100 mL), and again water (3 × 100 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel eluting with $CHCl_3$−CH_3OH, 95:5 to afford calix[4]arene amino acid **8** (1.0 g, 70%). ^{1}H NMR (DMSO-d_6) δ 8.21 (t, J = 5.7 Hz, 1 H), 8.03 (s, 1 H), 7.99 (s, 1 H), 7.83 (s, 2 H), 7.24 (d, J = 7.6 Hz, 1 H), 6.82 (s, 2 H), 6.81 (s, 2 H), 6.61 (s, 4 H), 5.9 (m, 2 H), 5.77 (t, J = 5.0 Hz, 2 H), 4.37 (d, J = 8.0 Hz, 2 H), 4.32 (d, J = 12.8 Hz, 2 H), 4.26 (d, J = 12.8 Hz, 2 H), 4.0 (m, 1 H), 3.76 (t, J = 7.3 Hz, 4 H), 3.71 (t, J = 7.3 Hz, 2 H), 3.61(s, 3 H), 3.2 (m, 2 H), 3.0 (m, 12 H), 1.37 (s, 9 H), 1.9−0.8 (6 × m, 65 H); FTIR ν 3332, 2930, 2859, 1654, 1559, 1474, 1219; MALDI-FTMS m/z 1419.9255 [(M + H)$^+$, calcd for $C_{79}H_{123}N_{10}O_{13}$ 1419.9265]. Anal. Calcd for $C_{79}H_{122}N_{10}O_{13}$: C, 66.83; H, 8.66; N, 9.86. Found: C, 66.44, H, 8.76, N, 9.67.

Scanning Electron Microscopy (SEM). The samples of **2** were prepared by a conventional procedure, previously described by Shinkai and co-workers.[21] The gel was obtained

in a flask and frozen in liquid nitrogen. The frozen specimen was dried in vacuo for 6 h and then coated with palladium–gold.

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