CO_2 in Supramolecular Chemistry: Preparation of Switchable Supramolecular Polymers

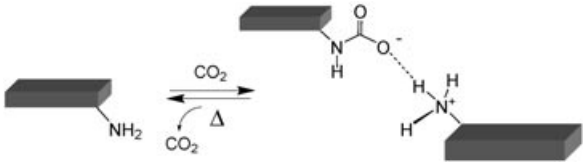
Heng Xu and Dmitry M. Rudkevich*[a]

Abstract: CO_2 gas was used to construct novel types of supramolecular polymers. Self-assembling nanostructures **11** and **13** were prepared, which employ both hydrogen bonding and dynamic, thermally reversible carbamate bonds. As precursors, calixarene ureas **1** and **2** were synthesized, which strongly aggregate/dimerize ($K_D \geq 10^6\ M^{-1}$ per capsule) in apolar solution with the formation of self-assembling capsules **7** and linear polymeric chains **8**, respectively, and also possess "CO_2-philic" primary amino groups on the periphery. CO_2 effectively reacts with molecules **7** and **8** in apolar solvents and cross-links them with the formation of multiple carbamate salt bridges. Oligomeric aggregate **11** and three-dimensional polymeric network **13** were prepared and characterized by ^1H and ^{13}C NMR spectroscopy. The morphology of supramolecular gel **13** was studied by scanning electron microscopy. Addition of a competitive solvent destroyed the hydrogen bonding in assembling structures **11** and **13**, but did not influence the carbamate linkers; carbamate salts **12** and **14**, respectively, were obtained. On the other hand, thermal release of CO_2 from **11** and **13** was easily accomplished (1 h, 100 °C) while retaining the hydrogen-bonding capsules. Thus, three-dimensional polymeric network **13** was transformed back to linear polymeric chain **8** without breaking up. Encapsulation and storage of solvent molecules by **11** and **13** was demonstrated. This opens the way for switchable materials, which reversibly trap, store, and then release guest molecules. A two-parameter switch and control over hydrogen bonding and CO_2–amine adducts was established.

Keywords: calixarenes · carbon dioxide fixation · self-assembly · supramolecular chemistry

Introduction

In this paper, application of CO_2 in supramolecular chemistry will be demonstrated. CO_2 circulates in the environment extensively through a number of processes known as the carbon cycle.[1] The development of novel methods of chemical fixation and utilization of this gas is ongoing,[2] and carbamate chemistry offers much potential in this direction. Generally unreactive, CO_2 readily combines with amines at ordinary temperatures and pressures to form carbamates, in which two amine molecules are held together by the salt bridge (Scheme 1).[3] The process is thermally reversible and can be considered as dynamic, covalent self-assembly.[4] With this in mind, we employed CO_2 as a cross-linking agent to build supramolecular polymeric materials. Supramolecular polymers represent a novel class of macromolecules, in which monomeric units are held together by reversible forces.[5]



Scheme 1. Reversible covalent chemistry between CO_2 and amines: self-assembly of molecular blocks.

Supramolecular polymers are self-assembling polymers, which form and dissipate by means of hydrogen bonds, metal–ligand interactions, and van der Waals forces. Thus, they combine features of conventional polymers with properties resulting from the bonding reversibility. Structural parameters of supramolecular polymeric materials, in particular their two- and three-dimensional architectures, can be switched "on–off" through the main chain assembly–dissociation processes. On the other hand, their strength and degree of polymerization relies on how tightly the monomeric units are aggregated. In this paper, we introduce a strategy to build supramolecular polymers that utilize hydrogen bonding and take advantage of the dynamic, reversible

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chemistry between CO_2 and amines. These polymers are also functional and possess multiple self-assembling capsules that may envelop guests. We demonstrate that subtle, two-parameter control over hydrogen bonding and CO_2–amine chemistry leads to switchable materials, which reversibly trap, store, and then release guest molecules. And finally, using CO_2, we convert linear supramolecular polymeric chains into supramolecular, three-dimensional polymeric networks. These are also switchable and can be transformed back to the linear chains without breaking up. Indeed, while supramolecular cross-linked polymers are known,[5] they break upon dissociation of the noncovalent aggregates, of which they are composed. Our materials are different in that they only release CO_2 and keep the hydrogen bonding intact.[6]

Results and Discussion

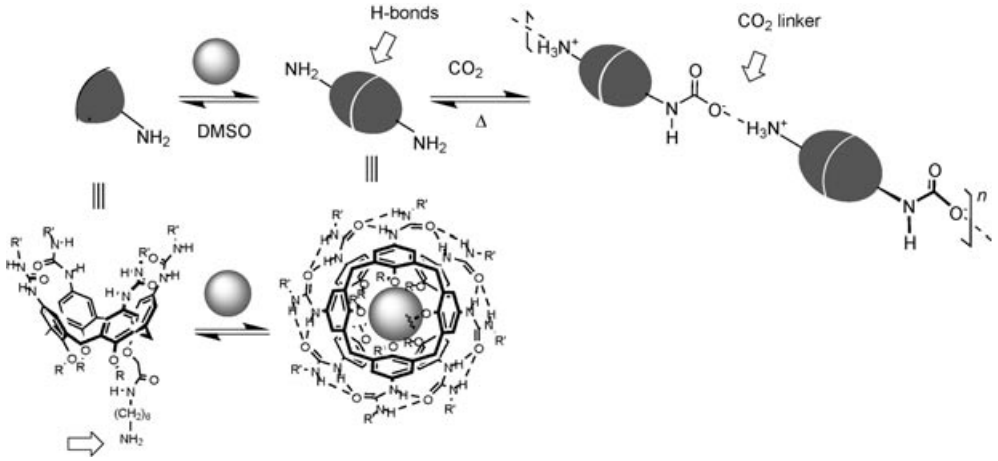
Design and synthesis: The chemistry between CO_2 and amines is essentially an acid–base equilibrium, and the formation of carbamate salts is thermally reversible.[3] CO_2 can typically be released by simple heating at $\geq 80\,^{\circ}C$. This property has been utilized in amine-based, reusable polymeric "CO_2 scrubbers".[7] Similarly, CO_2 can be trapped by amine-containing ionic liquids.[8] Thermally reversible carbamate chemistry has been recently employed for the preparation of organogels from long-chain alkyl amines.[9,10]

Our approach is sketched in Schemes 2 and 3 and introduces two generations of CO_2-based self-assembling nanostructures. Monomeric units were designed, which a) strongly aggregate/dimerize in apolar solution, b) possess "CO_2-philic" primary amino groups on the periphery, and c) form capsules upon self-assembly. For cross-linking, two such monomeric units were covalently attached with the appropriate orientation for linear, noncovalent polymerization (Scheme 3). The "CO_2-philic" amino groups were then introduced perpendicular to the main chain. In apolar solvents, once CO_2 is involved, multiple carbamate salt bridges should form resulting in either linear supramolecular aggregates (Scheme 2) or three-dimensional supramolecular networks (Scheme 3). Addition of a competitive solvent breaks the bonds formed from self-assembly but not the carbamate linkers. On the other hand, thermal release of CO_2 can be easily accomplished, but it does not influence the noncovalent aggregates and the capsules do not dissociate.

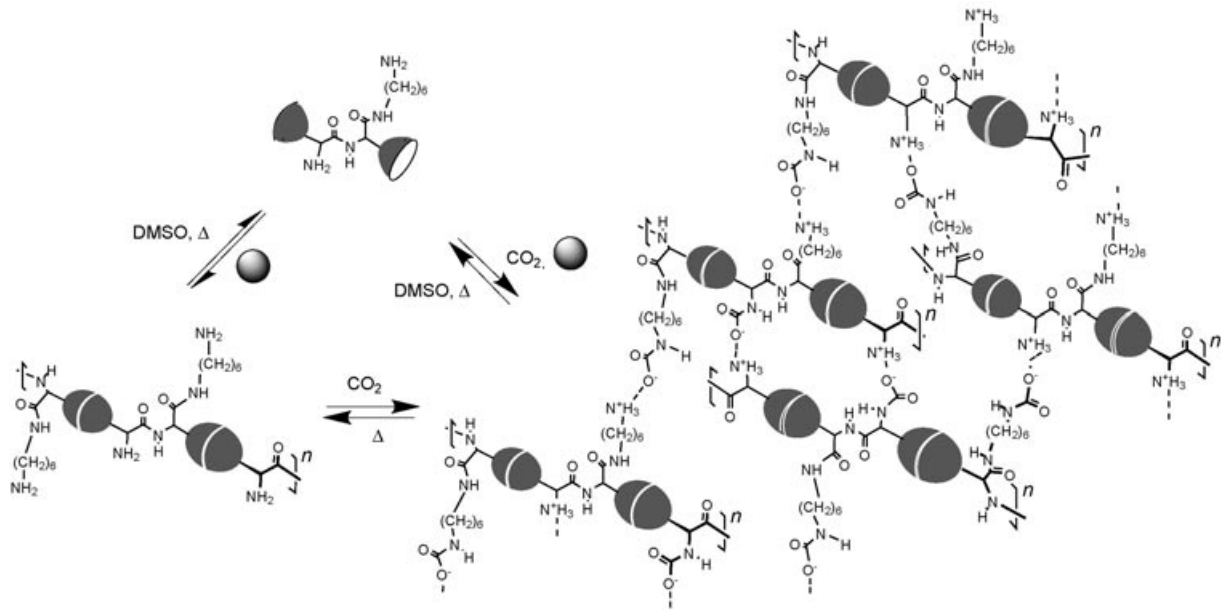
In the design of monomeric units, we took advantage of calixarenes as both self-assembling and cavity-forming modules.[11] Calix[4]arene tetraurea dimers were specifically chosen as these are probably the most-studied class of capsules.[11,12] Discovered almost ten years ago by Rebek[13] and Böhmer,[14] these capsules form in apolar solution ($K_D \geq 10^6\,M^{-1}$) and are held together by a seam of sixteen intermolecular C=O···H–N hydrogen bonds at the upper rims. This results in a rigid cavity of about 200 $Å^3$, which reversibly encapsulates one solvent molecule or a benzene-sized guest. When two calix[4]arene tetraurea compounds are covalently linked at their lower rims, hydrogen bonding yields supramolecular polymeric capsules.[15,16]

For this study, calix[4]arene tetraurea compounds **1** and **2** were synthesized, which possess "CO_2-philic" primary amino groups on the periphery (Scheme 4). Specifically, calixarene **1** is functionalized with a hexamethyleneamine fragment at its lower rim. In biscalix[4]arene **2**, two calixarene tetraurea moieties are linked with a dipeptide, di-L-lysine chain. Calixarenes were attached to the ε-NH_2 ends so that the di-lysine module orients them away from each other, in roughly opposite directions.[17,18] According to extensive molecular modeling, this also prevents the intramolecular assembly. The hexamethyleneamine chain was then attached to the carboxylic side of the dipeptide. This and the α-NH_2 group of **2** can react with CO_2, providing cross-linking.

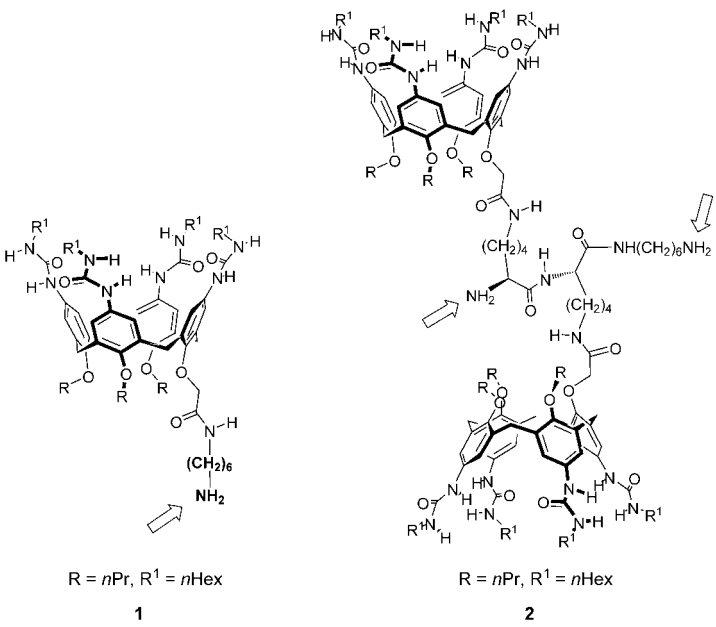
The key building block for the syntheses of **1** and **2** is calix[4]arene tetraurea acid **3**. It was prepared from known calixarene precursors in five steps starting with the parent tetrakis-*tert*-butyl calix[4]arene (Scheme 5).[15] Calixarene amine **1** was synthesized (as a TFA-salt; TFA = trifluoroacetic acid) from acid **3** and 1-N-Boc-protected 1,6-diaminohexane (*N*,*N*′-dicyclohexylcarbidiimide (DCC), 1-hydroxybenzotriazole (HOBt), Et_3N, DMF, 72 %; Boc = *tert*-butyloxycarbonyl), followed by deprotection with TFA (THF, 93 %).



Scheme 2. CO_2 linking calixarene capsules into a linear supramolecular polymer.



Scheme 3. CO_2 cross-links polymeric calixarene chains into a three-dimensional supramolecular network.



Scheme 4. Calixarene building blocks for supramolecular polymers. The "CO_2-philic" sites are marked.

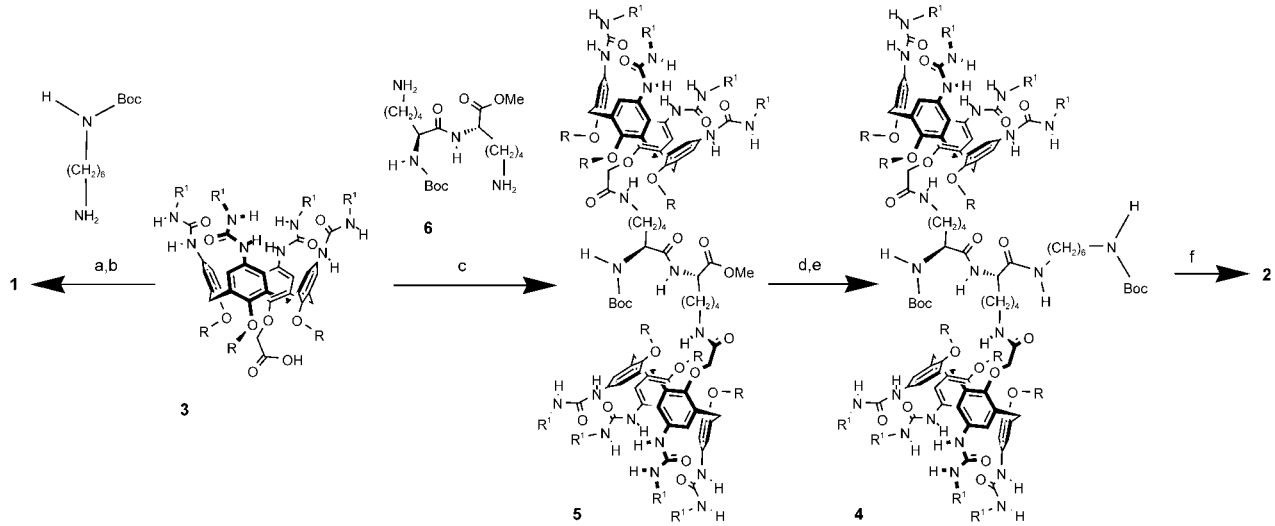
Biscalix[4]arene diamine **2** was prepared (as a TFA-salt) from bis-N-Boc-protected dipeptide **4** (THF, TFA, $>95\%$). Compound **4** was obtained from calix dipeptide methyl ester **5** by basic hydrolysis of the ester (LiOH, H_2O/THF, 91%), followed by reaction with 1-N-Boc-protected 1,6-diaminohexane (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI), HOBt, DMF, 76%). Dipeptide **5** was obtained by a conventional peptide coupling procedure from 2 equivalents of acid **3** and 1 equivalent of di-L-lysine **6** (EDCI, HOBt, DMF, 56%).[17] The amino groups in **1** and **2** were subsequently liberated from TFA by washing with aqueous NaOH solution.

Self-assembly: As expected,[13–15] calixarene tetraurea **1** dimerizes in apolar solution (^{1}H NMR, ESI-MS) with the formation of capsule **7** (Scheme 6). Due to the lack of symmetry in **7**, a multiple set of NH urea signals was recorded in C_6D_6, $CDCl_3$, and $CDCl_2CDCl_2$ between $\delta = 6.0$ and 8.5 ppm (for example, Figure 1a). These are characteristically shifted down field ($\delta \geq 2$ ppm), compared with model, non-dimerized ureas, showing the key features[13–15] of the capsule formation. Statistically, both a proximal and a distal regioisomer of **7** form, with respect to the orientation of the acetamide $OCH_2C(O)NH$ substituents at the lower rims of each calixarene capsule of **1**.[15] Moreover, the circular array of hydrogen bonds can be arranged either clockwise or counterclockwise. Capsule **7** dissociates to form monomeric tetraurea **1** in a more competitive solvent, [D_6]DMSO. This results in a much simpler ^{1}H NMR spectrum, reflecting the presence of a vertical symmetry plane in **1** (Figure 1b). For example, three ArNHC(O) urea singlets in a ratio of 1:1:2 at $\delta = 8.05$, 8.00, and 7.85 ppm and apparently three aromatic CH singlets in a ratio of 2:2:4 at $\delta = 6.81$, 6.79, and 6.61 ppm are clearly seen in the down-field part of the spectrum.

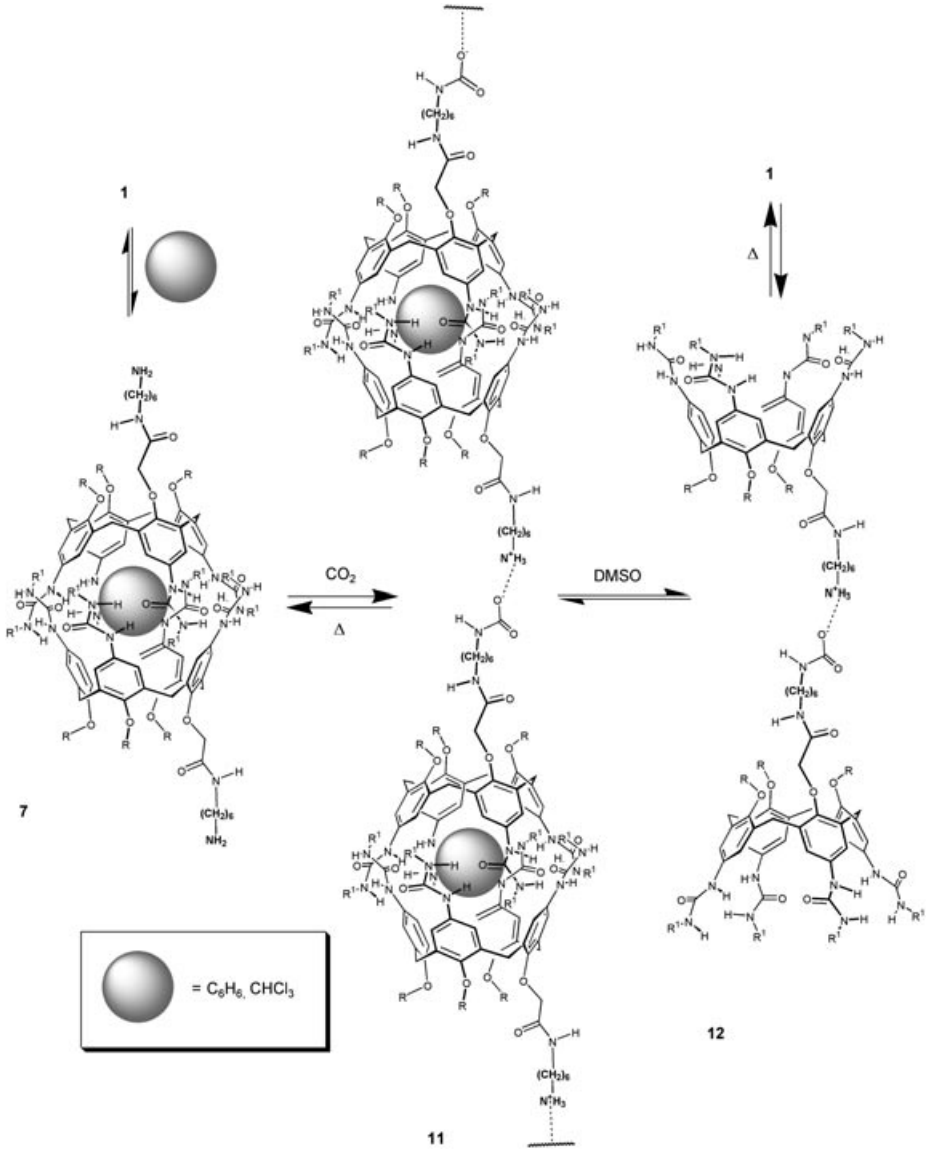
Having two calixarene modules for assembly, compound **2** and its immediate precursors **4** and **5** form linear supramolecular polymers **8**–**10** in apolar solution (Scheme 7).

Similar to **7**, multiple sets of NH urea signals were seen in the corresponding ^{1}H NMR spectra in $CDCl_3$ and C_6D_6. These were characteristically shifted down field (≥ 2 ppm; for example, Figure 2a).

With the dimerization constant $K_D \geq 10^6\,M^{-1}$ for each calixarene capsule,[19] an average degree of polymerization (DP) of at least 10^2 can be theoretically estimated for structures **8**–**10** at the NMR concentration range.[20] During the experiments, significantly increased viscosities were observed for solutions of biscalixarenes **2**, **4**, and **5** in $CHCl_3$ compared with the precursor **3**. While the relative viscosity



Scheme 5. a) DCC, HOBt, Et_3N, DMF, 24 h, 72 %. b) TFA, THF, 2 h, 93 %. c) EDCI, HOBt, DMF, 24 h, 56 %. d) LiOH, H_2O, THF, 12 h, 91 %. e) EDCI, HOBt, Et_3N, DMF, 24 h, 76 %. b) TFA, THF, 4 h, >95 %.



Scheme 6. Formation and dissociation of supramolecular aggregate **11**.

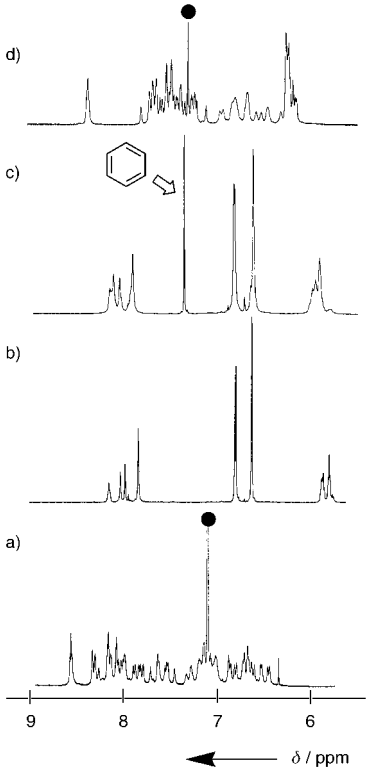


Figure 1. Downfield fragments of ^{1}H NMR spectra (500 MHz, 295 ± 1 K) of a) capsule **7** in C_6D_6, b) calixarene amine **1** in [D_6]DMSO, c) salt **12**, prepared upon dissociation of aggregate **11** in [D_6]DMSO; for this experiment, **11** was obtained upon bubbling CO_2 through a solution of **7** in benzene and thus entrapping benzene (the benzene signal is shown by an arrow), and d) aggregate **11**, obtained from CO_2 and **7** in $CHCl_3$/hexanes, 1:2 solution and redissolved in $CDCl_3$. The residual solvent signals are marked as ●.

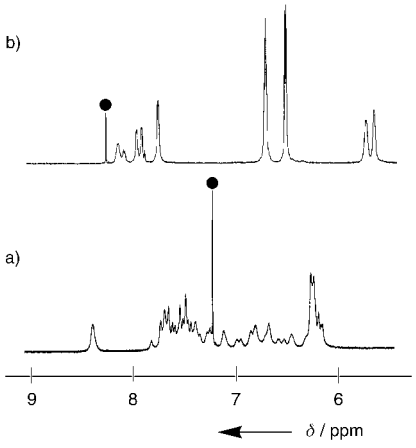


Figure 2. Downfield portions of ^{1}H NMR spectra (500 MHz, 295 ± 1 K) of a) polymeric capsules **10** in $CDCl_3$, b) biscalixarene **5** in [D_6]DMSO; this spectrum was obtained upon dissociation of **10** in [D_6]DMSO. The residual solvent signals are marked as ●.

of **3** is similar to the solvent and does not apparently change with changing the concentration, dramatic changes were detected for the biscalixarenes (≥5-fold, concentration range from 5 to 40 mM). Solutions of biscalixarene **2** were already viscous at the NMR concentrations (≈5 mM) and had to be diluted for further operations.

Specific viscosities (η_{sp}) of derivatives **1**, **3**, and **5** were measured as a function of concentration; the double-logarithmic plots are represented in Figure 3a. As expected, for

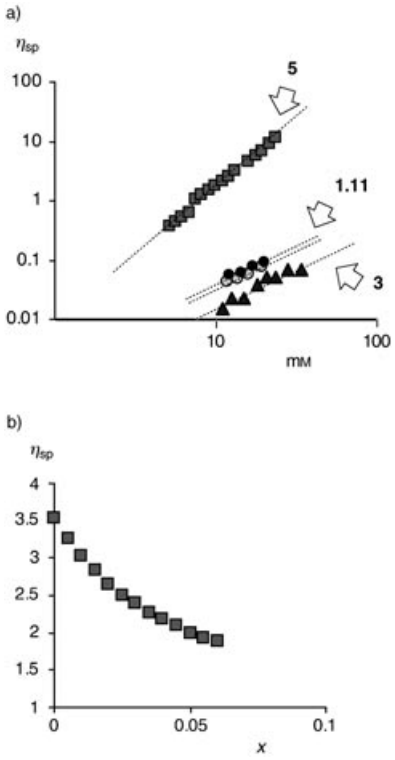
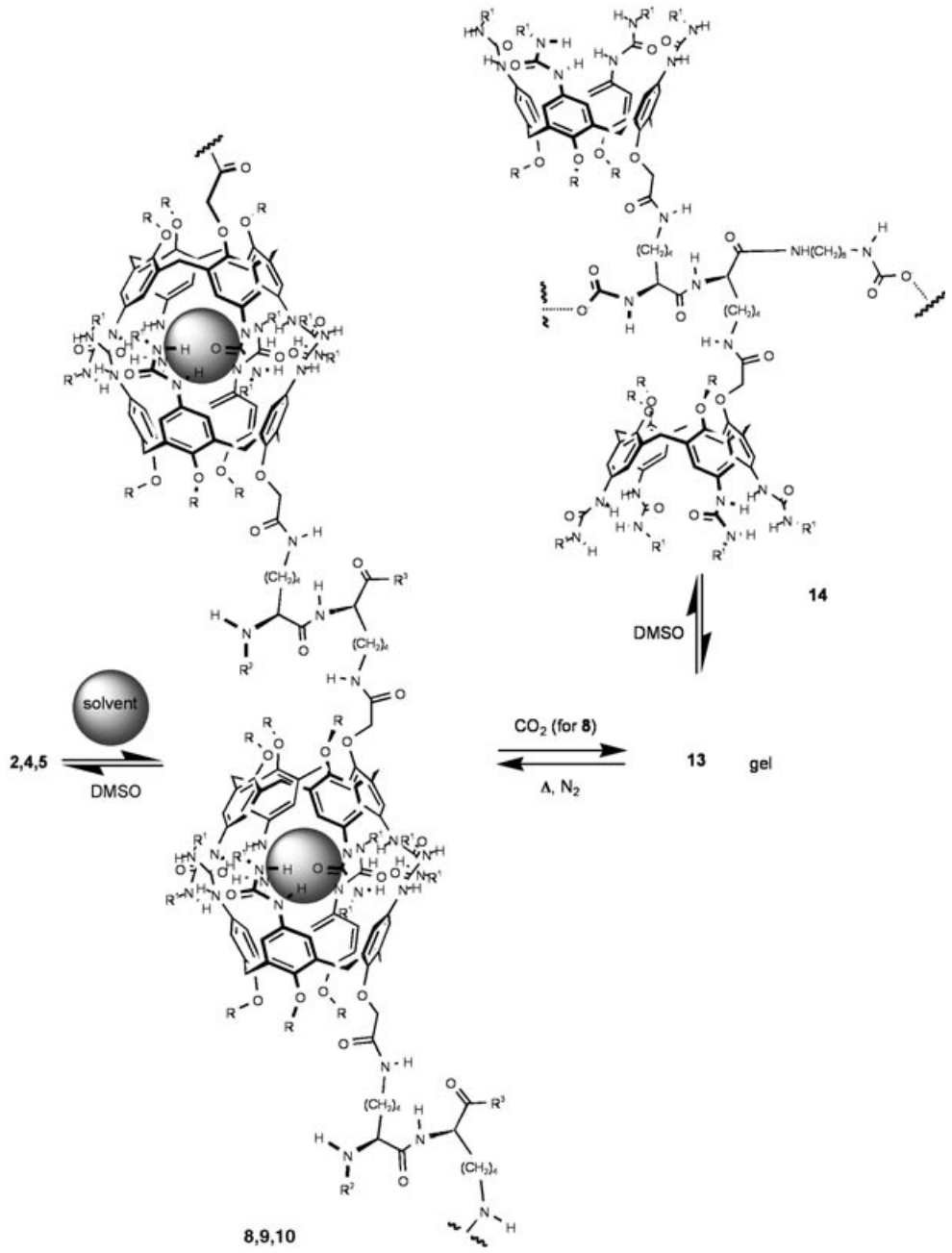


Figure 3. Viscosity measurements with calixarenes **3** and **5** in $CHCl_3$ and **1** and **11** in $CHCl_3$/benzene, ≈2:1 (295 ± 1 K): a) specific viscosities versus concentration (6–35 mM range), a double-logarithmic plot; b) effect of the addition of **3** (mole fraction x) on the specific viscosity of **5** at 20 mM. Viscosities of **1** and **11** in neat $CHCl_3$ (not shown) are similar, and comparable in value to calixarene **3**.

calixarenes **1** and **3** the viscosities are low and the plot has a slope of 1.1 ± 0.1. Such a linear relationship between η_{sp} and concentration indicates that only small aggregates (e.g., capsules) are formed, which are of constant size and apparently do not interact with each other. In contrast, the double-logarithmic relationship between η_{sp} and concentration for biscalixarene **5** exhibits a slope of ≈2; this implies the formation of reversibly breakable polymers, the size of which increases with concentration.[21] Due to steric restraints on the design of dipeptide chains, unimolecular cyclization of two calixarene tetraurea compounds in **2**, **4**, and **5** is not possible.

Addition of small quantities of calixarene **3** to a solution of biscalixarene **5** in $CHCl_3$ resulted in a dramatic decrease in viscosity (Figure 3b). Acting as a chain stopper, **3** may compete for hydrogen bonding with the calixarene fragments in **5** and its polymeric chains. Based on these viscosity measurements and using an approach developed by Meijer and co-workers,[21] the DP value for biscalixarene **5** of $\approx 2.8 \times 10^2$ was estimated at 20 mM, which corresponds to the average molar mass of $\approx 7.6 \times 10^5$ g mol^{-1}. When and 2 mol% of stopper **3** were used, the DP values dropped to 1.2×10^2 and 7.5×10^1, respectively. These observations once



Scheme 7. Formation and dissociation of linear supramolecular polymers **8–10** and cross-linked supramolecular material **13.** **8**: $R^2 = H$, $R^3 = NH(CH_2)_6NH_2$; **9**: $R^2 = Boc$, $R^3 = NH(CH_2)_6NHBoc$; **10**: $R^2 = Boc$, $R^3 = OMe$.

again confirm the reversibility of the described polymerization processes, which occur through multiple-capsule formation. Similar supramolecular polymerization phenomena are expected for structurally related biscalixarenes **2** and **4**.

The interiors of polymeric capsules **8–10** are most probably filled with solvent. As expected, **8–10** fully dissociate to monomeric units **2**, **4**, and **5** in polar [D_6]DMSO. Similar to **1**, this results in a much simpler ^{1}H NMR spectrum, reflecting the presence of the apparent vertical symmetry planes (e.g., Figure 2b).

Reactions with CO_2—first generation: Bubbling CO_2 through a solution of **7** in benzene caused a rapid precipitation of carbamate-linked supramolecular material, **11**. This belongs to the first generation. The chains in **11** are held together by calixarene hydrogen bonds and carbamate $CH_2N^+H_3\cdots O^-C(O)NHCH_2$ salt bridges (Scheme 6). Initially, one molecule of an amine reacts with CO_2 to form the corresponding carbamic acid. It is highly unstable and rapidly transfers the acidic proton to the second amine molecule, thus producing a relatively robust carbamate salt.[4] Formation of the carbamate bridges was confirmed by ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectrum of **1** in [D_6]DMSO, the terminal -CH_2NH_2 protons were seen as a triplet at $\delta = 2.53$ ppm ($J = 6$ Hz). For salt **12**, which is formed upon dissociation of polymer **11** in [D_6]DMSO, the

spectrum showed that these protons split in two 1:1 sets (-$CH_2N^+H_3$···$O^-C(O)NHCH_2$-): a triplet at $\delta = 2.58$ ppm ($J = 6.4$ Hz) for the first, and an apparent multiplet at $\delta \approx 2.9$ ppm for the second. These were assigned through NMR experiments with model alkyl amines, COSY, and from the literature.[4,10] A broad carbamate NH signal was detected at $\delta \approx 6$ ppm (^{1}H NMR, COSY). Resonance at $\delta \approx 160$ ppm in the ^{13}C NMR spectrum of **12** unambiguously identified the carbamic carbon atom (-HN−*C*(O)O^-). Notably, when amine **1** was treated with a large excess of CO_2 in [D_6]DMSO, the corresponding free carbamic acid formed, which was studied by ^{1}H, ^{13}C NMR, and COSY spectroscopy. For example, the HN−*C*OOH resonance was clearly seen at $\delta = 158$ ppm in the ^{13}C NMR spectrum. Free carbamic acids are still rare and elusive.[4,22,23]

Supramolecular material **11** is a colorless solid, soluble in chlorinated solvents, and insoluble in aromatic solvents. It was also obtained by the CO_2-induced precipitation from solutions of **7** in $CHCl_3$/hexanes, 1:2. A multiple set of the down-field NH urea signals of **11**, recorded in $CDCl_3$, clearly indicate the hydrogen-bonding assembly of polymeric chains (Figure 1d). At the same time, viscosities of capsules **7** and material **11**, obtained after the reaction with CO_2, appeared to be similar ($CHCl_3$ and $CHCl_3$/benzene, 2:1) (Figure 3a). These viscosities were low, apparently concentration independent (5–25 mM range), and comparable to relative viscosities of precursor **3**. Evidently, **11** is not significantly aggregated under these conditions.

The dimerization constant for each calixarene capsule of **11** is high,[19] and the carbamate–ammonium electrostatic interactions are also very strong in apolar solution.[4,8–10] These features do not allow the high concentrations of free end groups in structure **11**. On the other hand, carbamate–ammonium electrostatics is not directional and may offer significant flexibility to the resulting structures. We propose that for **11**, oligomeric rings rather than long polymeric chains are formed upon reaction of **7** with CO_2. The double-logarithmic plots of specific viscosities η_{sp} versus concentration obtained for monomer **1** and also polymer **11** in $CHCl_3$ are low and show slopes of approximately 1 (Figure 3a). Such linear relationships indicate that aggregates of constant size are formed, which do not interact with each other. Due to the low viscosity, these rings may not be large; we are currently studying their structure. We also noticed that chain–ring equilibrium posed a typical problem for supramolecular polymers and had been thoroughly analyzed by Meijer, Sijbesma, and co-workers.[21] The problem does not exist for preformed, linear supramolecular polymer **8**, for which CO_2 serves as a cross-linking agent.

Reactions with CO_2—second generation: Bubbling the gas through a solution of **8** in $CHCl_3$ or benzene yielded material **13**, which is a gel (Scheme 7). The main chains in **13** are held together by a hydrogen-bonding assembly of capsules and multiple carbamate -N^+H_3···$O^-C(O)NH$- bridges cross-link these chains. This is clearly a three-dimensional network, as the side amine groups are oriented in all three directions. Moreover, structure **8** possesses two types of amino group, and several possibilities for the carbamate formation exist (see for example, Scheme 3). Model experiments with CO_2 and simpler aliphatic amines[4,9,10] and ε-*N*-CBz-protected lysine (CBz = phenylmethoxycarbonyl) showed that these reactions readily occur.

Formation of the carbamate bridges was further confirmed by ^{13}C NMR spectroscopy. To be certain, we used $^{13}CO_2$ gas and prepared the ^{13}C-labeled gel **13**. In the ^{13}C NMR spectrum of diamine **2** (in [D_6]DMSO), prior to the reaction four C=O carbonyl signals were clearly detected: three for the amide fragments at $\delta = 175.4$, 171.7, and 169.4 ppm, and one, intense signal for the upper-rim urea compounds at $\delta = 155.8$ ppm (Figure 4a). In the spectrum of

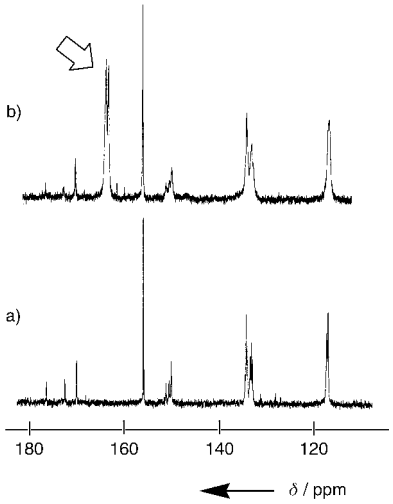


Figure 4. Portions of ^{13}C NMR spectra (125 MHz, [D_6]DMSO, 295 ± 1 K) of a) biscalixarene **2**, b) carbamate salt **14** obtained upon dissociation of ^{13}C-labeled gel **13**. The gel was prepared from **2** and $^{13}CO_2$ in $CHCl_3$. The carbamate ^{13}C-labeled signals are marked. For the corresponding ^{1}H NMR spectra, see Figure 5.

the ^{13}C-labeled salt **14** (which is formed upon dissociation of the ^{13}C-labeled polymer **13** in [D_6]DMSO), in addition to these signals, two new singlets of high intensity appeared at $\delta = 163.5$ and 162.8 ppm (Figure 4b). We attribute these singlets to the carbamate α-HN-$^{13}C(O)O^-$ and $(CH_2)_6$HN-$^{13}C(O)O^-$ groups. Notably, these two signals disappeared after heating solution **14** for 1 h at ≈100 °C and bubbling N_2 through it.

The ^{1}H NMR spectra of material **13** is difficult to obtain, which is clearly due to the cross-linked structure and numerous possibilities for forming carbamic bridges. However, the same trend as for the simpler oligomer **11** can be clearly observed (compare Figure 5 with Figures 1 and 2). Rather similar to capsule **7**, multiple sets of NH urea signals were seen in the corresponding ^{1}H NMR spectra of precursor **2** in $CDCl_3$; viscous polymer **8** was formed (Figure 5a). These NH signals were characteristically shifted down field. As expected, **8** fully dissociated to monomeric **2** in polar [D_6]DMSO (Figure 5b). Similar to **1**, this resulted in a simplified ^{1}H NMR spectrum, reflecting the apparent vertical symmetry plane in the molecule. Being insoluble in apolar solvents, material **13** readily dissociated in DMSO to form a mixture of carbamate salts of type **14**. The corresponding

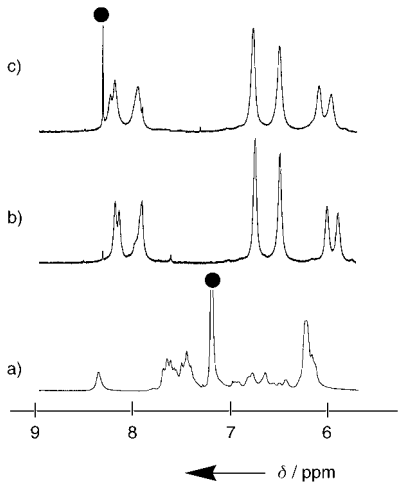


Figure 5. Downfield portions of ^{1}H NMR spectra (500 MHz, 295 ± 1 K) of a) calixarene **2** in $CDCl_3$ (e.g., polymeric chain **8**), b) calixarene **2** in [D_6]DMSO, c) salt **14**, prepared upon dissociation of polymeric gel **13** in [D_6]DMSO; for this experiment, polymer **13** was obtained upon bubbling CO_2 through a solution of **2** in $CHCl_3$ (e.g., **8**). The $CHCl_3$ signal is marked as ●.

^{1}H NMR spectrum resembles those for carbamate salt **12** (Figure 5c and Figure 1c).

Properties: Self-assembling materials **11** and **13** exhibit unique properties. They assemble and dissipate in a two-parameter fashion, upon changing either the solvent polarity or temperature. The calixarene capsules completely dissociate in DMSO, so only carbamate salts **12** and **14** can be detected (Figure 1c and Figure 5c, respectively). Salts **12** and **14** most probably undergo further solvolysis generating loose ion pairs. The carbamate C–N bonds are not broken under these conditions, however, they can be dismantled upon heating, thus releasing CO_2. In the case of **12**, in apolar solution monomeric capsules of type **7** form, and in DMSO free amine **1** is regenerated. For **14** in apolar solution, linear hydrogen-bonded polymer **8** forms, and in DMSO biscalixarene **2** is completely regenerated. In both cases, carbamate polymers **11** and **13** can be reconstructed by simply reintroducing CO_2.

Another interesting feature of materials **11** and **13** is their multiple capsules. These are already preformed in apolar solutions, but then convert into solids/gels upon exposure to CO_2. Upon completing this CO_2-initiated polymerization, they trap guest molecules and transport them to the solid state; this results in guest storing materials.

In a preliminary test, obtained from benzene and carefully dried polymer (0.1 mm Hg, RT, 24 h), **11** did not release benzene when the capsules were intact. In a suspension of **11** in noncompetitive [D_{10}]*p*-xylene, no trace of benzene was detected (^{1}H NMR, 500 MHz), but when [D_6]DMSO was used, polymeric capsules of type **11** dissociated and released visible quantities of benzene, approximately one molecule per capsule (Figure 1c). We fully expect similar behavior from gel **13**. However, in addition to being encapsulated, guest/solvent molecules are entrapped within the gel's three-dimensional network[24] (see for example, Figure 5c). So far, $CHCl_3$ and benzene have been gelated, and we are currently studying other solvents and guests.

To obtain visual insight into the aggregation mode and morphology in **13**, dry samples were prepared for scanning electron microscopy (SEM) analysis. While its precursor **8** only shows the formation of negligible fibers, a three-dimensional network is obvious for **13**. Figure 6 displays typical pictures obtained from the xerogel of **13**.

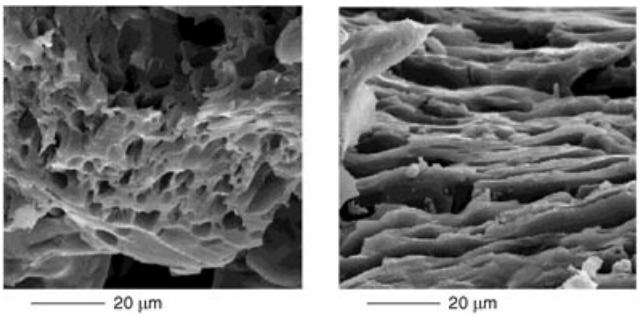


Figure 6. SEM pictures of xerogel **13** obtained upon bubbling CO_2 through a solution of **8** in $CHCl_3$(bar 20 μm).

Conclusion

In summary, CO_2 can be used to build supramolecular polymers and polymeric materials. These utilize hydrogen bonding and take advantage of the dynamic, reversible chemistry of CO_2. Subtle, two-parameter control over noncovalent and covalent forces can be achieved. This leads to switchable materials. Their dynamics and structural characteristics can be controlled on a molecular level. These polymers also possess multiple, self-assembling capsules that may envelop guests. The most immediate applications are in encapsulation, and we are currently testing the ability of our materials to entrap, store, and release chemicals into reaction mixtures. We are also exploring supramolecular, three-dimensional polymeric networks. Their morphology and mechanical properties can be manipulated by reversible switching to form the corresponding linear polymeric chains without breaking hydrogen bonds by the simple thermal release of CO_2.[25] With synthetic variations of the polymeric chains, particularly their geometry and stereochemistry and also side-chain functionalization, more possibilities are open for the use of CO_2 in supramolecular chemistry and nanochemistry. Simultaneously, we are looking at supramolecular applications of other gases.[26]

Experimental Section

General: Melting points were determined on a Mel-Temp apparatus (Laboratory Devices, Inc.) and are uncorrected. ^{1}H, ^{13}C NMR, and COSY spectra were recorded at 295 ± 1 °C on a JEOL Eclipse 500 MHz spectrometer. Chemical shifts were measured relative to residual, nondeuterated solvent resonances. FTIR spectra were recorded on a Bruker Vector 22 spectrometer. ESI-MS spectra were obtained on a Finnigan LCQ Ion Trap apparatus. MALDI-TOF mass spectra were recorded on a delayed extraction MALDI-TOF mass spectrophotometer Voyager DE

(Applied Biosystems). HRMS MALDI spectra were obtained on an Ion Spec Ultima FTMS. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. SEM images were obtained by using a JEOL 35C microscope.

All experiments with moisture- and/or air-sensitive compounds were carried out under a dried nitrogen atmosphere. For column chromatography, Silica Gel 60 Å was used (Sorbent Technologies, Inc.; 200–425 mesh). Parent tetrahydroxycalix[4]arene[27] and other calixarene precursors[15] were prepared according to the published procedures. Molecular modeling was performed using commercial MacroModel 7.1 with Amber* Force Field.

Calix[4]arene tetraurea acid (3): *n*-Hexyl isocyanate (1.78 mL, 12.25 mmol) was added to a solution of the previously described tetraaminocalix[4]arene[15] (2.0 g, 2.45 mmol) in dry CH_2Cl_2 (80 mL), and the reaction mixture was stirred at RT for 4 h. The solvent was removed in vacuo, and the residue was triturated with hexane to yield the tetraurea ester as a tan powder (2.72 g, 2.25 mmol, 92%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.06 (s, 1H), 8.05 (s, 1H), 7.81 (s, 2H), 6.87 (s, 2H), 6.84 (s, 2H), 6.53 (m, 4H), 5.88 (m, 2H), 5.69 (t, J = 5.0 Hz, 2H), 4.71 (s, 2H), 4.50 (d, J = 13.3 Hz, 2H), 4.29 (d, J = 12.37 Hz, 2H), 4.12 (q, J = 7.3 Hz, 2H), 3.75 (t, J = 7.8 Hz, 2H), 3.68 (t, J = 7.8 Hz, 2H), 3.62 (t, J = 7.8 Hz, 2H), 3.15–2.90 (m, 12H), 1.92 (m, 2H), 1.82 (m, 4H), 1.5–0.80 ppm (6×m, 56H).

A mixture of the tetraurea ester (1.5 g, 1.2 mmol) and KOH (0.67 g, 12.0 mmol) in THF/H_2O, (5:1, 60 mL) was placed under reflux overnight, after which H_2O (60 mL) was added, and the pH was adjusted to 2 with aqueous HCl (1 M). The product was extracted with $CHCl_3$ (3×60 mL), the organic layer was dried over Na_2SO_4, evaporated, and recrystallized from MeOH to give tetraurea acid **3** as a yellowish powder (1.13 g, 80%). M.p. >300 °C; ^{1}H NMR ([D$_6$]DMSO): δ = 8.07 (s, 1H), 8.03 (s, 1H), 7.83 (s, 2H), 6.87 (s, 4H), 6.59 (s, 4H), 5.88 (m, 2H), 5.72 (t, J = 5.0 Hz, 2H), 4.56 (s, 2H), 4.43 (d, J = 12.6 Hz, 2H), 4.27 (d, J = 12.6 Hz, 2H), 3.76 (t, J = 7.8 Hz, 2H), 3.69 (t, J = 7.8 Hz, 2H), 3.67 (t, J = 7.8 Hz, 2H), 3.01 (m, 8H), 2.95 (m, 4H), 1.95–1,75(m, 6H), 1.5–1.1 (m, 32H), 1.0–0.8 ppm (m, 21H); ^{13}C NMR ([D$_6$]DMSO): δ = 171.5, 155.8, 151.1, 150.4, 150.2, 135.6, 135.3, 135.1, 134.8, 134.3, 134.1, 118.7, 77.5, 77.2, 71.2, 31.7, 30.4, 30.3, 26.7, 23.1, 23.0, 22.7, 14.4, 10.8, 10.5 ppm; FTIR (KBr): $\tilde{\nu}$ = 3376, 3333, 2961, 2931, 2858, 1761, 1654, 1558, 1478, 1213 cm^{-1}; MALDI-FTMS: m/z: calcd for $C_{67}H_{101}N_8O_{10}$: 1177.7635; found: 1177.7632 $[M+H]^+$.

Calixarene (1): N-Boc-1,6-diaminohexane (0.38 mL, 1.68 mmol), DCC (0.35 g, 1.68 mmol), HOBt (0.23 g, 1.68 mmol), and Et_3N (0.23 mL, 1.68 mmol) were added to a stirred and ice-cooled solution of **3** (1.0 g, 0.84 mmol) in DMF (30 mL). The mixture was stirred for 30 min at 0 °C and for 24 h at RT, then filtered, concentrated in vacuo, diluted with $CHCl_3$, and washed successively with $NaHSO_4$ (1 N, 4×100 mL), water (3×100 mL), $NaHCO_3$ (1 N, 4×100 mL), and again with water (3×100 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was separated chromatographically on silica gel eluting with $CHCl_3$/CH_3OH (95:5) to afford the N-Boc-protected amine **1** as a colorless solid (0.84 g, 72%). M.p. 185 °C (decomp); ^{1}H NMR ([D$_6$]DMSO): δ = 8.17 (t, J = 5.7 Hz, 1H), 8.02 (brs, 1H), 7.98 (brs, 1H), 7.83 (brs, 2H), 6.81 (s, 2H), 6.79 (s, 2H), 6.76 (t, J = 5.5 Hz, 1H), 6.62 (brs, 4H), 5.82 (m, 2H), 5.77 (t, J = 5.3 Hz, 2H), 4.35 (s, 2H), 4.33 (d, J = 12.6 Hz, 2H), 4.27 (d, J = 12.6 Hz, 2H), 3.76 (t, J = 7.3 Hz, 4H), 3.72 (t, J = 7.3 Hz, 2H), 3.24 (m, 2H), 3.00 (m, 12H), 2.91 (m, 2H), 1.36 (s, 9H), 1.9–0.8 ppm (5×m, 71H); ^{13}C NMR ([D$_6$]DMSO): δ = 169.2, 156.1, 155.74, 155.7, 151.2, 150.7, 150.3, 135.4, 135.1, 135.0, 134.5, 134.2, 134.1, 118.7, 118.4, 77.8, 77.3, 76.5, 74.8, 31.6, 30.4, 28.83, 28.8, 26.7, 23.0, 22.9, 22.7, 14.5, 10.63, 10.6 ppm; FTIR (KBr): $\tilde{\nu}$ = 3329, 2928, 2852, 1628, 1559, 1476, 1213 cm^{-1}.

A solution of the N-Boc-protected **1** (0.5 g, 0.36 mmol) in THF (15 mL) was treated with TFA (5 mL) and stirred at RT for 2 h. The reaction mixture was concentrated in vacuo to afford the pure TFA salt of **1** (0.47 g, 93%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.18 (t, J = 5.5 Hz, 1H), 8.05 (s, 1H), 7.99 (s, 1H), 7.84 (s, 2H), 6.80 (s, 2H), 6.63 (s, 2H), 6.60 (s, 2H), 5.88 (m, 2H), 5.78 (t, J = 5.5 Hz, 2H), 4.37 (s, 2H), 4.32 (d, J = 12.8 Hz, 2H), 4.26 (d, J = 12.8 Hz, 2H), 3.75 (t, J = 7.2 Hz, 4H), 3.71 (t, J = 7.2 Hz, 2H), 3.26 (m, 2H), 3.0 (m, 12H), 2.78 (m, 2H), 1.9–0.8 ppm (5×m, 70H); ^{13}C NMR ([D$_6$]DMSO): δ = 169.4, 155.8, 151.3, 150.7, 150.4, 135.3, 135.1, 135.0, 135.0, 134.5, 134.2, 134.0, 118.8, 118.54, 118.5, 77.3, 76.6, 74.8, 31.6, 30.4, 27.6, 26.6, 26.2, 22.9, 22.7, 14.5, 10.7, 10.6 ppm; FTIR (KBr): $\tilde{\nu}$ = 3339, 2932, 2859, 1659, 1599, 1562, 1468, 1213 cm^{-1}; ESI-MS: m/z: calcd for $C_{75}H_{115}F_3N_{10}O_{11}$: 1389; found: 1389.

The TFA salt (0.50 g, 0.36 mmol) in $CHCl_3$ (100 mL) was washed with aqueous 10% NaOH (2×50 mL), then evaporated and dried in high vacuo. ^{1}H NMR ([D$_6$]DMSO): δ = 8.18 (t, J = 5 Hz, 1H), 8.05 (brs, 1H), 8.00 (brs, 1H), 7.85 (brs, 2H), 6.80 (2×s, 4H), 6.61 (s, 4H), 5.88 (m, 2H), 5.80 (t, J = 5.5 Hz, 2H), 4.36 (s, 2H), 4.32 (d, J = 12.8 Hz, 2H), 4.26 (d, J = 12.8 Hz, 2H), 3.76 (t, J = 7.8 Hz, 4H), 3.69 (t, J = 7.8 Hz, 2H), 3.22 (m, 2H), 2.99 (m, 12H), 2.53 (t, J = 6.0 Hz, 2H), 1.9–1.7, 1.6–1.4, 1.4–1.3, 1.3–1.1, 1.0–0.8 ppm (5×m, 67H); ^{13}C NMR ([D$_6$]DMSO): δ = 169.3, 155.8, 155.7, 151.2, 150.7, 150.4, 135.4, 135.1, 135.0, 134.5, 134.2, 134.1, 118.8, 118.7, 118.5, 118.47, 77.3, 76.5, 74.8, 31.6, 30.4, 26.7, 22.9, 22.7, 14.5, 10.6 ppm; FTIR (KBr): $\tilde{\nu}$ = 3344, 2930, 2858, 1654, 1559, 1475, 1213 cm^{-1}; ESI MS: m/z: calcd for $C_{73}H_{114}N_{10}O_9$: 1275; found: 1276 $[M+H]^+$, 2552 $[2M+2H]^+$.

Di-L-lysine (6):[28,18] To a stirred and ice-cooled solution of *N*-ε-Cbz-L-lysine TFA salt (1.0 g, 2.45 mmol) in DMF (30 mL), Et_3N (0.34 mL, 2.45 mmol) was added. Then, after 15 min, acid *N*-α-Boc-*N*-ε-Cbz-L-lysine (0.93 g, 2.45 mmol), HOBt (0.66 g, 4.90 mmol), and DCC (1.01 g, 4.90 mmol) were successively added. The mixture was stirred for 30 min at 0 °C and for 24 h at RT, then filtered, concentrated under reduced pressure, diluted with EtOAc (200 mL), and washed successively with $NaHSO_4$ (1 N, 4×50 mL), water (3×50 mL), $NaHCO_3$ (1 N, 4×50 mL), and again with water (3×50 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was separated chromatographically on silica gel eluting with THF/hexanes (2:3) to afford the desired Cbz-protected dipeptide (1.14 g, 71%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.10 (d, J = 7.3 Hz, 1H), 7.34 (m, 10H), 7.22 (t, J = 5.5 Hz, 2H), 6.78 (d, J = 8.0 Hz, 1H), 4.99 (s, 4H), 4.20 (m, 1H), 3.90 (m, 1H), 3.59 (s, 3H), 2.96 (m, 4H), 1.32 (s, 9H), 1.8–1.1 ppm (4 m, 12H); ^{13}C NMR ($CDCl_3$): δ172.8, 172.7, 156.8, 156.0, 136.7, 136.6, 128.6, 128.57, 128.3, 128.2, 128.2, 80.1, 66.8, 66.7, 54.1, 52.4, 52.1, 40.5, 32.2, 31.6, 29.4, 29.2, 28.4, 22.6, 22.3 ppm; FTIR (KBr): $\tilde{\nu}$ = 3359, 3036, 2948, 1699, 1544, 1259 cm^{-1}.

A solution of the Cbz-protected dipeptide (0.2 g, 0.30 mmol) in CH_3OH (10 mL) was treated with 10% Pd/C (20 mg) and stirred under an H_2 atmosphere for 6 h. The mixture was filtered through Celite and concentrated under reduced pressure to give product **6** as an oil (0.11 g, 94%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.28 (d, J = 7.3 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 4.22 (m, 1H), 3.93 (m, 1H), 3.62 (s, 3H), 2.72 (t, J = 7.1 Hz, 4H), 1.36 (s, 9H), 2.0–1.0 ppm (m, 12H); MALDI-TOF MS: m/z: calcd for $C_{18}H_{36}N_4O_5$: 388.5; found: 388.8 $[M]^+$.

Biscalixarene (5): Calixarene tetraurea acid **3** (1.0 g, 0.84 mmol), EDCI (0.32 g, 1.68 mmol), and HOBt (0.23 g, 1.68 mmol) were added to a stirred and ice-cooled solution of dipeptide **6** (0.16 g, 0.42 mmol) in DMF (30 mL). The mixture was stirred 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 separated chromatographically on silica gel eluting with $CHCl_3$/CH_3OH (9.5:0.5) to afford calix dipeptide **5** (0.64 g, 56%). M.p. >18 °C (decomp); ^{1}H NMR ([D$_6$]DMSO): δ = 8.19 (m, 2H), 8.12 (d, J = 7.8 Hz, 1H), 8.02 (s, 1H), 8.01 (s, 1H), 7.97 (s, 1H), 7.96 (s, 1H), 7.81 (s, 2H), 7.80 (s, 2H), 6.79 (s, 2H), 6.78 (s, 4H), 6.77 (s, 2H), 6.59 (s, 4H), 6.58 (s, 4H), 5.84 (m, 4H), 5.76 (m, 4H), 4.33 (brs, 4H), 4.30 (d, J = 12.4 Hz, 4H), 4.23 (d, J = 12.4 Hz, 4H), 3.91 (m, 1H), 3.72 (t, J = 6.9 Hz, 8H), 3.68 (t, J = 6.9 Hz, 4H), 3.58 (s, 3H), 3.20 (m, 4H), 3.08–2.90 (m, 24H), 1.34 (s, 9H), 1.9–0.8 ppm (6×m, 130H); ^{13}C NMR ([D$_6$]DMSO): δ = 173.0, 172.9, 169.3, 155.74, 155.7, 151.25, 151.2, 150.7, 150.3, 135.3, 135.16, 135.1, 135.0, 134.5, 134.46, 134.2, 134.1, 134.0, 118.8, 118.72, 118.5, 118.4, 78.5, 77.3, 76.5, 74.8, 54.5, 52.3, 32.3, 31.6, 31.4, 31.2, 30.4, 30.1, 29.9, 28.7, 26.7, 23.6, 23.4, 23.0, 22.9, 22.7, 14.5, 10.6 ppm; FTIR (KBr): $\tilde{\nu}$ = 3333, 2931, 2858, 1653, 1559, 1213, 1042, 965 cm^{-1}; MALDI-FTMS: m/z: calcd for $C_{152}H_{232}N_{20}O_{23}Na$: 2728.7491; found: 2728.7671 $[M+Na]^+$; ESI-MS: m/z: calcd for $C_{152}H_{232}N_{20}O_{23}Cl$: 2741; found: 2743 $[M+Cl]^-$.

Biscalixarene (4): A mixture of **5** (2 g, 0.74 mmol), THF (25 mL), and aqueous LiOH (1 N, 10 mL) was stirred overnight at RT, after which H_2O (30 mL) was added, and the pH was adjusted to 6 with aqueous 1 M HCl. The product was extracted with $CHCl_3$ (3×60 mL). The organic layer was dried over Na_2SO_4 and evaporated to give the tetraurea acid (1.81 g,

91%). M.p. >300°C; ^{1}H NMR ([D$_6$]DMSO): δ=8.22 (brs, 2H), 8.09 (brs, 2H), 7.99 (brs, 2H), 7.93 (d, J=7.8 Hz, 1H), 7.83 (brs, 4H), 6.83 (s, 2H), 6.82 (s, 4H), 6.81 (s, 2H), 6.62 (s, 4H), 6.61 (s, 4H), 5.85 (m, 4H), 5.78 (m, 4H), 4.35 (brs, 4H), 4.33 (d, J=13.3 Hz, 4H), 4.22 (d, J=13.3 Hz, 4H), 4.19 (m, 1H), 3.94 (m, 1H), 3.75 (t, J=6.9 Hz, 8H), 3.69 (t, J=6.9 Hz, 4H), 3.22 (m, 4H), 3.10–2.90 (m, 24H), 1.34 (s, 9H), 1.9–0.8 ppm (6×m, 130H); ^{13}C NMR ([D$_6$]DMSO): δ=174.1, 172.7, 169.3, 155.8, 151.3, 151.2, 150.7, 150.3, 135.4, 135.2, 134.9, 134.4, 134.2, 134.0, 118.8, 118.5, 78.5, 77.3, 76.5, 74.8, 67.6, 54.7, 52.2, 31.7, 31.5, 31.2, 30.4, 30.1, 30.0, 28.7, 26.7, 25.7, 23.7, 23.4, 23.0, 22.9, 22.6, 14.4, 10.6 ppm; FTIR (KBr): $\tilde{\nu}$=3349, 2930, 1664, 1560, 1472, 1367, 1216 cm^{-1}.

N-Boc-1,6-diaminohexane (0.17 mL, 0.74 mmol), EDCI (0.14 g, 0.74 mmol), HOBt (0.10 g, 0.74 mmol), and Et_3N (0.10 mL, 0.74 mmol) were added to a stirred and ice-cooled solution of the above-mentioned acid (1.0 g, 0.37 mmol) in DMF (20 mL). The mixture was stirred for 30 min at 0°C and for 24 h at RT, filtered, concentrated, diluted with $CHCl_3$, and washed successively with $NaHSO_4$ (1N, 3×80 mL), water (2×80 mL), $NaHCO_3$ (1N, 3×80 mL), and again with water (3×80 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was separated chromatographically on silica gel eluting with $CHCl_3$/CH_3OH (94:6) to afford **4** (0.81 g, 76%). M.p. >185°C (decomp); ^{1}H NMR ([D$_6$]DMSO): δ=8.20 (brs, 2H), 8.04 (brs, 2H), 8.00 (brs, 2H), 7.87 (brs, 1H), 7.82 (s, 4H), 7.73 (d, J=7.8 Hz, 1H), 6.98 (d, J=7.3 Hz, 1H), 6.82 (s, 2H), 6.81 (s, 4H), 6.80 (s, 2H), 6.73 (t, J=7.1 Hz, 1H), 6.61 (s, 4H), 6.60 (s, 4H), 5.87 (m, 4H), 5.78 (m, 4H), 4.35 (s, 4H), 4.32 (d, J=12.8 Hz, 4H), 4.26 (d, J=12.8 Hz, 4H), 3.87 (m, 1H), 3.74 (t, J=6.9 Hz, 8H), 3.70 (t, J=6.9 Hz, 4H), 3.21 (m, 4H), 3.00 (m, 24H), 2.86 (m, 4H), 1.36 (s, 9H), 1.34 (s, 9H), 1.9–0.8 ppm (6×m, 138H); ^{13}C NMR ([D$_6$]DMSO): δ=172.4, 171.6, 169.3, 169.29, 156.1, 156.0, 155.8, 151.3, 151.2, 150.7, 150.3, 135.4, 135.2, 135.0, 134.4, 134.2, 134.0, 118.7, 118.5, 118.45, 78.6, 77.7, 77.3, 76.5, 74.8, 55.2, 52.9, 39.2, 39.0, 31.6, 31.5, 30.4, 30.0, 29.5, 28.8, 28.7, 26.7, 26.5, 23.8, 23.3, 23.0, 22.9, 22.7, 14.4, 10.6, 10.57 ppm; FTIR (KBr): $\tilde{\nu}$=3325, 2929, 2864, 1659, 1556, 1471, 1214 cm^{-1}.

Biscalixarene (2): A solution of **5** (0.2 g, 0.07 mmol) in THF (20 mL) was treated with TFA (20 mL) and then stirred at RT for 4 h. The reaction mixture was concentrated in vacuo to afford the pure TFA-salt of **2**. The salt 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 **2** (0.18 g, 96%). ^{1}H NMR ([D$_6$]DMSO): δ=8.22 (brs, 4H), 8.17 (brs, 2H), 8.01 (brs, 1H), 7.94 (brs, 5H), 6.82 (s, 2H), 6.81 (s, 4H), 6.80 (s, 2H), 6.56 (s, 4H), 6.55 (s, 4H), 6.07 (brs, 4H), 5.97 (brs, 4H), 4.35 (s, 4H), 4.33–4.19 (m, 8H), 4.14 (m, 1H), 3.80–3.60 (m, 12H), 3.22 (m, 4H), 3.10–2.90 (m, 26H), 1.90–0.80 ppm (5×m, 138H); ^{13}C NMR ([D$_6$]DMSO): δ=175.4, 171.7, 169.4, 155.9, 155.8, 151.3, 150.7, 150.3, 135.4, 135.2, 135.0, 134.4, 134.2, 133.9, 133.89, 118.9, 118.8, 118.6, 77.3, 76.5, 74.8, 55.3, 52.6, 31.6, 30.4, 29.6, 28.7, 26.9, 26.7, 23.3, 23.1, 22.7, 22.6, 14.5, 10.6 ppm; FTIR (KBr): $\tilde{\nu}$=3340, 2928, 2863, 1657, 1557, 1470, 1213 cm^{-1}; MALDI-TOF: m/z: calcd for $C_{152}H_{236}N_{20}O_{20}Na$: 2712.8; found: 2712.0 $[M+Na]^+$; ESI-MS: m/z: calcd for $C_{152}H_{237}N_{20}O_{20}$: 2691; found: 2692 $[M+H]^+$.

Supramolecular oligomer (11) and salt (12): Calixarene **1** (0.50 g, 0.39 mmol) in benzene (6 mL) was placed in a glass tube (13×100 mm) and dry CO_2 was then bubbled through the solution for 5 min at 35°C. Oligomer **11** quantitively precipitated, was filtered off, and dried under vacuum at RT. The experiment was performed at least five times giving reproducible results. Upon dissolution in DMSO, material **11** dissociated to give carbamate salt **12**. M.p. >140°C (decomp); ^{1}H NMR ([D$_6$]DMSO): δ=8.18 (2×brs, 4H), 8.11 (brs, 2H), 7.96 (brs, 4H), 6.89 (2×s, 8H), 6.66 (s, 8H), 6.00 (brs, 2H), 5.95 (brs, 2H), 5.91 (brs, 4H), 5.80 (brs, 1H), 4.42 (s, 4H), 4.37 (d, J=12.4 Hz, 4H), 4.29 (d, J=12.4 Hz, 4H), 3.77 (m, 12H), 3.26 (m, 4H), 3.04 (m, 26H), 2.58 (t, J=6.4 Hz, 2H), 1.9–1.7, 1.7–1.5, 1.4–1.3, 1.3–1.1, 1.0–0.8 ppm (5×m, 134H); ^{13}C NMR ([D$_6$]DMSO): δ=169.3, 159.8, 155.8, 151.3, 150.8, 150.3, 135.5, 135.2, 135.1, 134.5, 134.2, 134.0, 134.0, 118.8, 118.6, 77.3, 76.5, 74.8, 31.7, 31.5, 30.4, 27.1, 26.7, 23.0, 22.9, 22.7, 14.4, 10.6, 10.59 ppm.

Supramolecular polymer (13) and carbamate salts (14): Diamine **2** (0.2 g, 0.07 mmol) in $CHCl_3$ (5 mL) was placed in a glass tube (13×100 mm) and dry CO_2 ($^{13}CO_2$) was then bubbled through the solution for 3 min at RT. Material **13** formed as a gel, which was then dried under high vacuum at RT. The experiment was performed at least five times giving reproducible results. Upon dissolution in DMSO, material **13** dissociated to form carbamate salts of type **14**. ^{1}H NMR ([D$_6$]DMSO): δ=8.27 (brs), 8.22 (brs), 8.12–7.90 (brs), 6.90–6.70 (brs), 6.70–6.50 (brs), 6.14 (brs), 6.02 (brs), 4.36 (brs), 4.25 (m), 3.90–3.60 (m), 3.50–3.30 (m), 3.22 (m), 3.15–2.85 (m), 1.85–1.70 (m), 1.59–1.53 (m), 1.33 (m), 1.23 (m), 0.95–0.85 ppm (m); ^{13}C NMR ([D$_6$]DMSO): δ=175.5, 171.8, 169.4, 163.3, 162.9, 155.9, 151.4, 150.8, 150.3, 135.4, 135.2, 134.9, 134.4, 134.1, 133.8, 118.9, 118.6, 77.4, 76.3, 74.5, 31.6, 30.4, 26.7, 23.4, 23.1, 22.9, 22.7, 14.5, 10.6 ppm.

SEM: Samples of **8** and **13** were prepared by a conventional procedure, previously described by Shinkai and co-workers.[29] The gel was placed in a flask and frozen in liquid nitrogen. The frozen specimen was dried in vacuo for 24 h and then coated with palladium-gold.

Viscosity: Viscosity measurements for calixarenes **1**–**5**, **7**, and **11** in $CHCl_3$ and $CHCl_3$/benzene were performed in a standard glass viscometer using conventional protocols.[30] All experiments were performed at least twice showing good reproducibility. The DP values for biscalixarene **5** in the presence of chain stopper **3** were estimated using an earlier-derived equation (see below),[21a] assuming that the dimerization constant K_D for a calixarene tetraurea capsule[19] was 10^6 M^{-1}:

$$DP = \frac{2([\mathbf{5}]+[\mathbf{3}])}{[\mathbf{3}]-\frac{1}{4K_D}[1-\sqrt{1+8K_D([\mathbf{3}]+2[\mathbf{5}])}]}$$

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