

Carbon dioxide and supramolecular chemistry

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Concepts and techniques of supramolecular chemistry are applied to the century-old chemistry between CO₂ and amines to design novel sensing systems and nanoscale, self-assembling polymeric materials and networks.

Introduction

In this article, we will revisit traditional chemistry of carbon dioxide (CO₂) and introduce novel strategies for CO₂ chemical sensing, fixation and utilization. These are based on supramolecular chemistry—chemistry of intermolecular interactions and reversible assemblies.

CO₂ is one of the major greenhouse gases.¹ It circulates in the environment through a variety of processes known as the *carbon cycle*. Large-scale industrial processes, volcanoes and living systems release huge quantities of CO₂ into the atmosphere. On the other hand, plants and also oceans, lakes, and rivers collect it. Still, CO₂ in the atmosphere is accumulating much faster than the Earth's natural processes can absorb it. The CO₂ levels in the atmosphere have risen by more than 30% over the last 250 years and these concentrations may well double or even triple in the next century. Such extensive CO₂ circulation in atmosphere, industry and agriculture requires not only its systematic monitoring under a variety of conditions, but more importantly, necessitates the development of improved methods for CO₂ chemical utilization.²

It has been known for decades that CO₂ readily reacts with amines under ordinary conditions to yield carbamates, presumably by way of the corresponding carbamic acids (Fig. 1).³ In recent years, carbamates have been successfully employed in preparative organic chemistry. They have been

converted to isocyanates⁴ or effectively reacted with alkyl halides to yield urethanes,^{5,6} thus providing an alternative synthetic equivalent to highly toxic phosgene. Carbamates are thermally unstable and release CO₂ upon heating. Accordingly, polymer-bound amines have been employed in industry as reusable “CO₂ scrubbers”, removing CO₂ from industrial exhaust streams.⁷ It has been demonstrated that an amine-containing ionic liquid also traps CO₂.⁸ Imprinted polymers have been introduced, in which a template can be attached and then removed through a carbamate linker.⁹ Finally, reactions between CO₂ and immobilized amines have been employed for gas sensing.¹⁰

In our laboratory, we promote a supramolecular approach to the problem. For example, a nanostructured material, presented in Fig. 2, employed CO₂ and is a polycarbamate.¹¹ This is a so-called supramolecular polymer. It is reversibly assembled from multiple components, switchable, gels various solvents, and even contains self-assembling, hydrogen bonding capsules for guest entrapment. It can even be further functionalized to show interesting optical properties. More of these structures, essentially based on CO₂, will follow. In particular, we will revisit the mechanism of carbamate formation and show its implications to CO₂ sensing. The chemistry between CO₂ and amines will then be used to construct switchable supramolecular polymers, self-assembling materials and nanoscale architectures. Functionalization and applications of such materials will be explored. Reversibly formed polymeric capsules for entrapment, separation, storage and controlled release of guest molecules will be introduced. Taken together, these advances may help begin a new page in supramolecular chemistry of this and other atmospheric and industrial gases.¹²

Carbamic acids and fluorimetric CO₂ sensing

Bubbling CO₂ through a solution of 1-(aminomethyl)pyrene 1 (Fig. 3), in polar aprotic solvents, such as DMSO and DMF, resulted in significant (>10 times) increase in the fluorescence emission (λ_{em} = 408 nm, λ_{ex} = 341 nm).¹³ We found, that the species responsible for the observed fluorescence was free

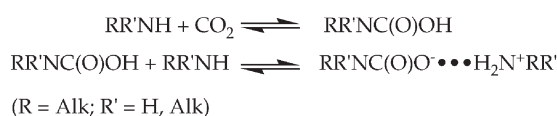


Fig. 1 Reversible carbamate chemistry.

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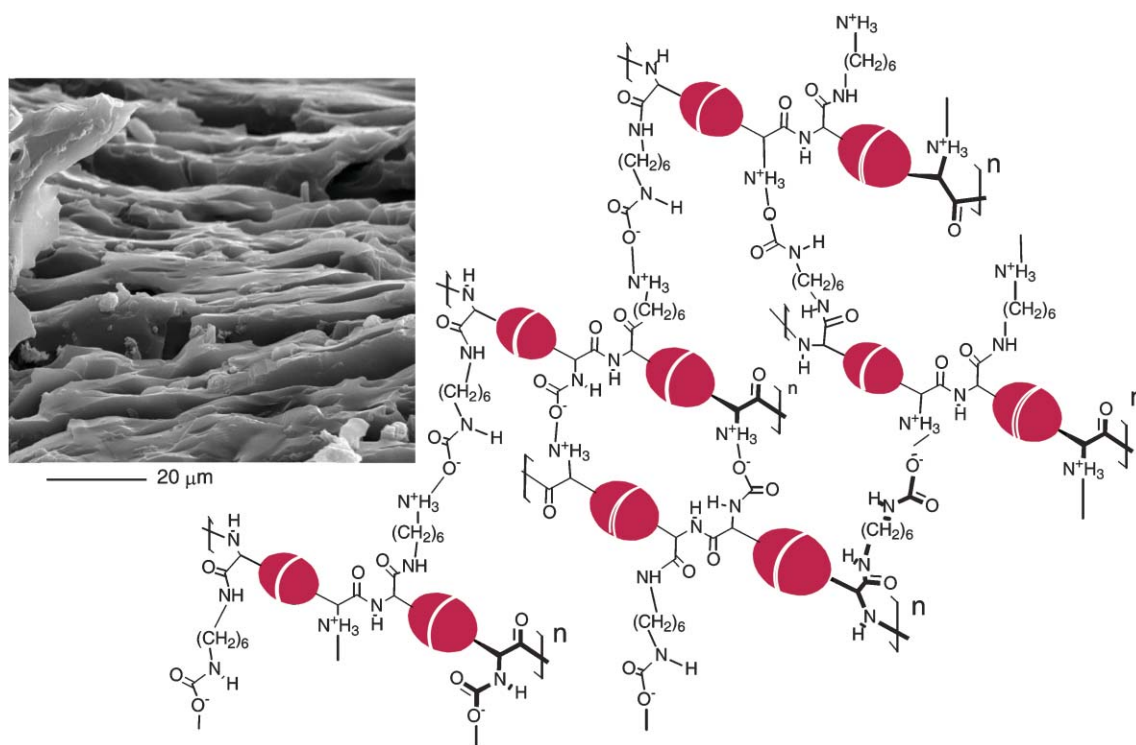


Fig. 2 CO₂ is used as a cross-linking agent in supramolecular polycarbamate networks. Upper-left: SEM image of the reversibly formed polycarbamate gel.¹¹

carbamic acid **2**. This was quite unexpected, considering that carbamic acids are highly unstable. Itself, amine **1** only weakly emits fluorescence under ambient conditions. This is due to photo-induced electron transfer (PET) quenching of the excited fluorophore by the intramolecular amino group lone pair. We suggested, that upon the reaction with dissolved CO₂, carbamic acid **2** is formed, in which PET quenching is no longer possible. The lone pair of electrons on the nitrogen atom is now involved in a conjugation with the carbonyl oxygen. This leads to an overall increase in observed fluorescence. PET of this type has been known and well exploited for pH sensing.¹⁴ Bubbling N₂ through solutions of **2** resulted in loss of fluorescence.

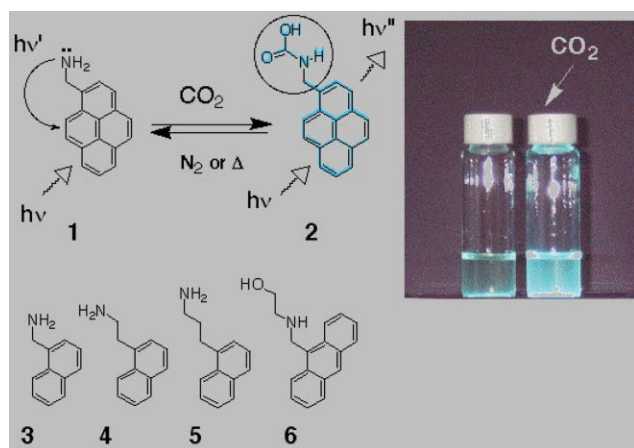


Fig. 3 Fluorescent sensing of CO₂ with amines **1**, **3**–**6**. In the experiment, depicted on the photo, aminomethylpyrene **1** in DMF was measured.¹³

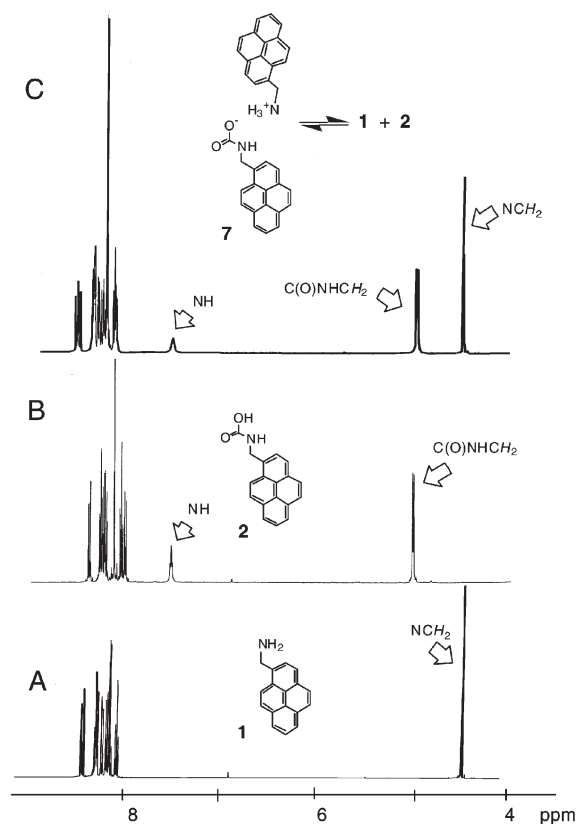


Fig. 4 CO₂ induced spectral changes of aminomethylpyrene **1**.¹³ ¹H NMR spectra (in DMSO-*d*₆, 295 K) of: (A) compound **1**; (B) **1** after saturation with CO₂, formation of carbamic acid **2**; (C) independently prepared carbamate salt **7**.

Similar behavior was recently documented for many other amines (for example, **3–6**, Fig. 3), which possess fluorophore fragments, separated from the NH_2 group by one or even more methylene units.^{13,15,16}

The reactions between amine **1**, **3–5** and CO_2 were monitored by NMR, and free carbamic acids were detected in all cases.^{13,16} They appeared to be reasonably stable in polar, aprotic solution and were characterized by ^1H , ^{13}C NMR and, in some cases, IR spectroscopy. For example, aminomethylpyrene **1** cleanly reacted with CO_2 (10–15 equiv. in $\text{DMSO-}d_6$) in the NMR tube to form carbamic acid **2** (Fig. 4).¹³ Prior to CO_2 exposure, benzylic protons of **1** were seen as a singlet at 4.46 ppm. After CO_2 bubbling, these were transformed into a doublet ($J = 6$ Hz) at 4.91 ppm. A very broad signal appeared at ~ 10.6 ppm, which was assigned to the C(O)OH . The carbamate NH signals also emerged as a triplet ($J = 6$ Hz) at 7.54 ppm. Furthermore, a resonance at 158.1 ppm in the ^{13}C NMR spectrum identified the carbamic (C=O) carbon atom. The loss of CO_2 can be achieved by simply flushing the NMR solution with N_2 or other inert gas at room or, more effectively, elevated temperatures.

Over the years, carbamic acids, with $\text{NH}_2\text{C(O)OH}$ as the simplest representative, have been the subject of considerable speculation. They are very important in mechanistic organic chemistry. They are suggested as intermediates in the

formation and decomposition of carbamates, hydrolysis of isocyanates, in the Hofmann and Curtius rearrangements. Carbamic acids might also form in biological systems in the presence of CO_2 . In early, rare cases, carbamic acids were detected by somewhat unconventional methods.³ Composite ices of NH_3 , H_2O , and CO_2 have been studied by IR, suggesting the formation of carbamic acid upon irradiation with a 1 MeV proton source.¹⁷ Protonated carbamic acids have been characterized by Olah and co-workers under superacidic conditions.¹⁸ More recently, carbamic acids have been detected and used as protecting groups in organic syntheses involving amines in supercritical CO_2 ($sc\text{CO}_2$).¹⁹ In one spectacular case, the solid-state structure of dibenzylamine carbamic acid $\text{Bz}_2\text{NC(O)OH}$ has been published.²⁰ Our studies demonstrated that free carbamic acids can be obtained, handled and studied in traditional solvents under ordinary laboratory conditions.

Self-assembly of carbamates

Carbamic acids easily transform to carbamate salts (Fig. 1). Carbamate salts $\text{RNHC(O)O}^- \text{H}_3\text{N}^+\text{R}$ from amines **1,3–5** were prepared by simply bubbling CO_2 through their solutions in apolar solvents such as CHCl_3 or benzene.^{13,16} Under these conditions, they quantitatively precipitate. Carbamate salts are typically soluble only in polar solvents.

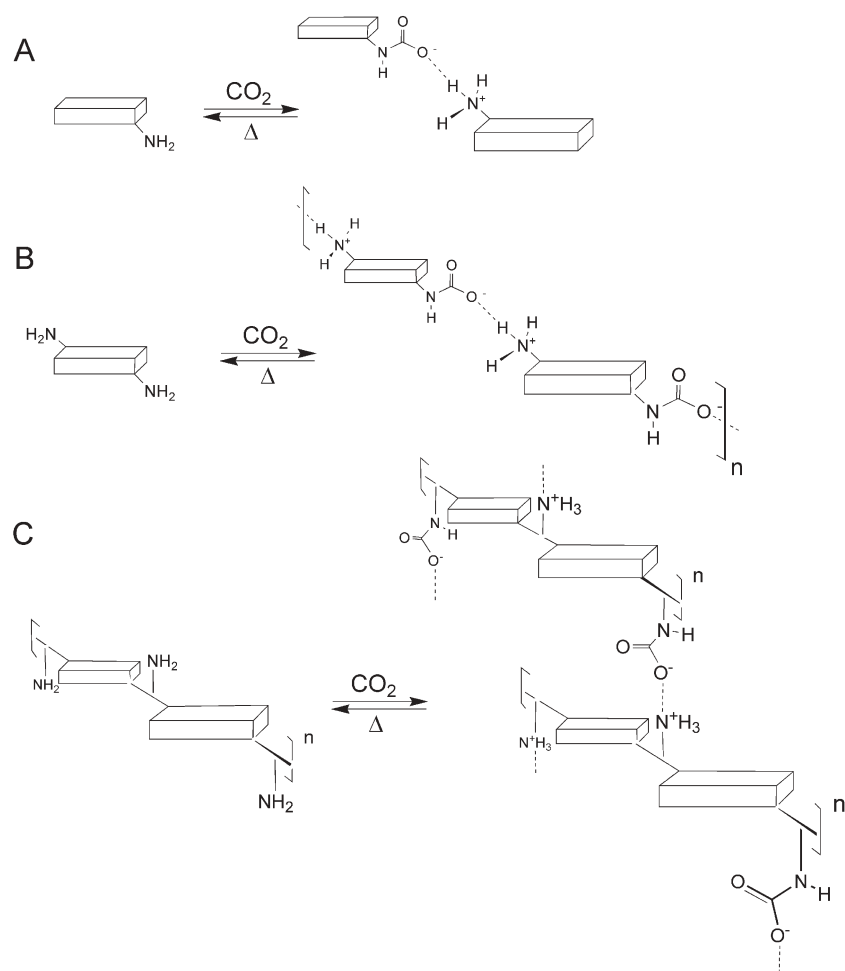


Fig. 5 Reversible covalent chemistry between CO_2 and amines. Self-assembly of molecular blocks leads to dimers (case A), linear (case B) and cross-linked polymers (case C).

The chemistry is essentially an acid–base equilibrium (proton transfer) between an initially formed free carbamic acid and a second amine. The NMR features of carbamate salts are quite different from their carbamic acids. For example, in the ^1H NMR spectrum of carbamate salt **7** in $\text{DMSO-}d_6$ benzylic protons were recorded as *two* separate signals, a singlet at 4.48 and a doublet at 4.90 ppm ($J = 5.5$ Hz). The carbamate NH signal was seen as a triplet ($J = 5.5$ Hz) at 7.53 ppm (Fig. 4).¹³ Recent IR data has suggested that in polar, aprotic solvents carbamates may reversibly transform back into the corresponding free carbamic acids and amines.¹⁶ Carbamates easily release CO_2 and the starting amines simply upon brief refluxing in aromatic solvents.

Reversible carbamate chemistry may thus be considered as another case of *dynamic, covalent self-assembly of building blocks* (Fig. 5). Compound **7** is one example of such assemblies, possessing two fluorophores in close proximity. There are more examples now. Weiss showed, that exposure of long-chain primary RNH_2 ($\text{R} = \text{C}_{10}\text{H}_{21}$, $\text{C}_{12}\text{H}_{25}$, $\text{C}_{14}\text{H}_{29}$, $\text{C}_{16}\text{H}_{33}$, $\text{C}_{18}\text{H}_{37}$) and secondary $\text{RR}'\text{NH}$ ($\text{R} = \text{R}' = \text{C}_8\text{H}_{17}$, $\text{C}_{18}\text{H}_{37}$) alkyl amines to CO_2 results in the formation of thermally responsive alkylammonium alkylcarbamate organogels.²¹ The amine precursors here are called “latent” gelators because they alone do not gelate liquids: the sol–gel transformation is affected only by CO_2 . In another example, the amine containing ionic liquid 1-(3'-aminopropyl)-3-butylimidazolium tetrafluoroborate reacted with CO_2 with

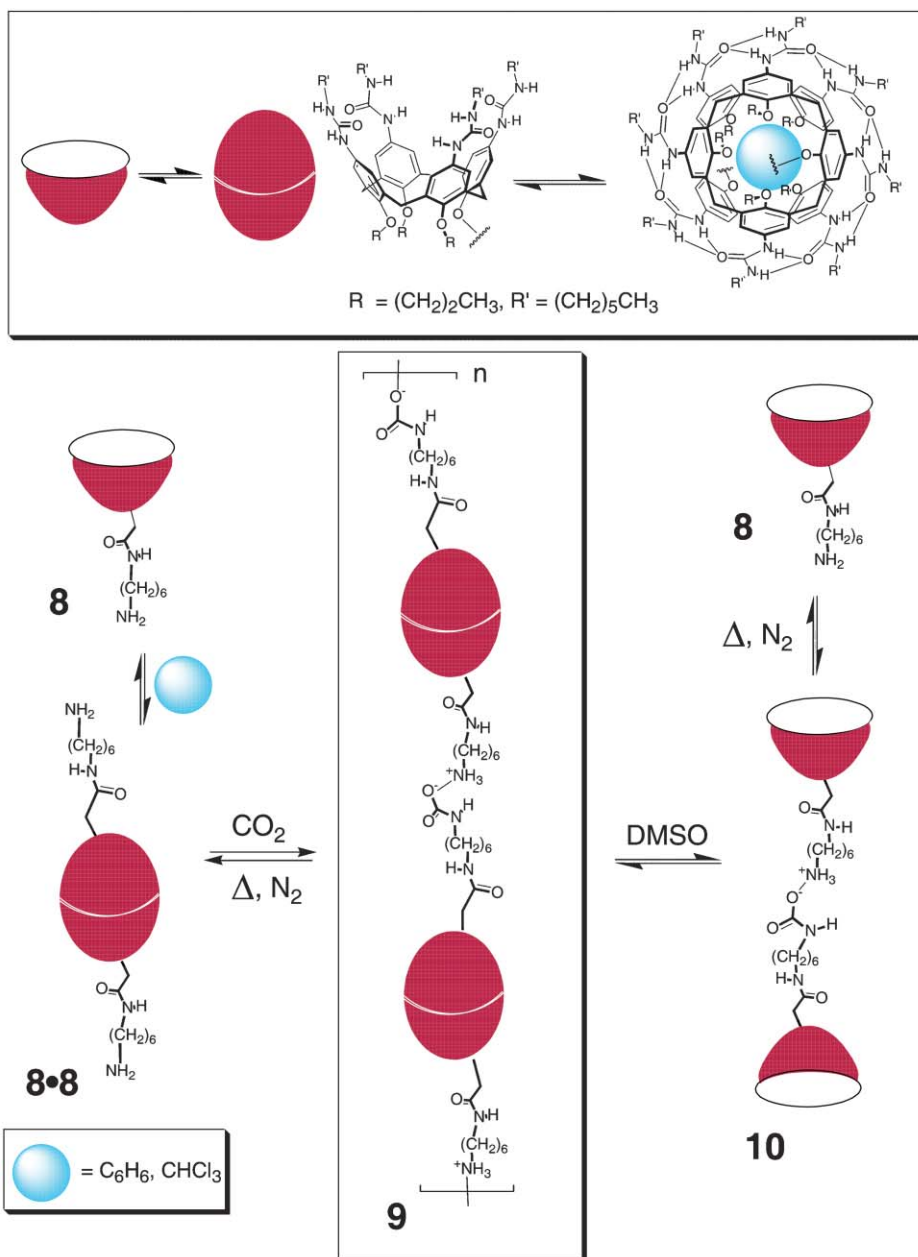


Fig. 6 Formation of linear supramolecular polymer **9** includes self-assembly of capsules **8–8** and their reaction with CO_2 . Polymeric chains **9** dissociate in DMSO.

the formation of the corresponding carbamate dimers.⁸ This process can be used to capture CO₂ in purification of industrial gas mixtures.

Dynamic covalent chemistry (DCC) is now quickly emerging as a promising alternative to non-covalent self-assembly.²² It simply offers an elegant opportunity of performing supramolecular chemistry with covalent bonds. One of the most important advantages here is the robustness of covalently organized structures, which on the other hand can be reversibly broken, at will. We suggested that carbamate bonds could be employed for a wider variety of DCC experiments.¹³

Very interesting are reactions between CO₂ and di- or even polyamines, since they can lead to reversibly formed polymeric chains or even cross-linked 3D networks (Fig. 5B and 5C). In one case, such structures have been proposed for polycarbamate $[-\text{H}_3\text{N}^+(\text{CH}_2)_{12}\text{NHC}(\text{O})\text{O}^- - \text{H}_3\text{N}^+(\text{CH}_2)_{12}\text{NHC}(\text{O})\text{O}^-]_n$, which forms thermally reversible organogels.²¹

Reversibly formed polymers are usually called supramolecular polymers.²³ They represent a novel class of macromolecules, in which monomeric units are held together by reversible bonds/forces. These are self-assembling polymers, and thus far hydrogen bonds, metal–ligand interactions, and van der Waals forces have been employed to construct them. Supramolecular polymers 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 association–dissociation processes. On the other hand, their strength and degree of polymerization depend on how tightly the monomeric units are aggregated.

We introduced a strategy to build supramolecular polymeric chains (see Fig. 5B), which takes advantage of dynamic chemistry between CO₂ and amines *and* also utilize hydrogen bonds.²⁴

Monomeric units were designed, which (a) strongly aggregate/dimerize in apolar solution and (b) possess “CO₂-philic” primary amino groups on the periphery. Calixarenes were employed as self-assembling units. Calix[4]arene tetraurea dimers are probably the most studied class of strong hydrogen bonding aggregates.²⁵ Discovered ten years ago by Julius Rebek^{26,27} and Volker Boehmer,²⁸ these dimers form in apolar solution with $K_D \geq 10^6 \text{ M}^{-1}$ and are held together by a seam of sixteen intermolecular C=O to H–N hydrogen bonds. This results in a rigid inner cavity of $\sim 200 \text{ \AA}^3$, which reversibly encapsulates a solvent molecule or a benzene-sized guest

For initial studies, calix[4]arene tetraurea **8** was synthesized, which possesses CO₂-philic primary amino groups on the periphery (Fig. 6).²⁴ This calixarene dimerized in apolar solution with the formation of capsule **8–8**. The process can be monitored by ¹H NMR spectroscopy and also ESI mass spectrometry. Due to the lack of symmetry in dimeric structure **8–8**, a multiple set of NH urea signals was recorded in C₆D₆, CDCl₃, and CDCl₂CDCl₂ between 6 and 8.5 ppm (for example, Fig. 7A). These are characteristically shifted downfield ($\Delta\delta \geq 2 \text{ ppm}$), compared to model, non-dimerized ureas. Capsule **8–8** dissociates to monomeric tetraurea **8** in more competitive DMSO-*d*₆. This results in a simpler ¹H NMR spectrum, reflecting the presence of a vertical symmetry plane in **8** (Fig. 7B). For example, three ArNHC(O) urea singlets in a

ratio 1 : 1 : 2 at 8.1, 8.0, and 7.9 ppm are clearly seen in the downfield part of the spectrum.

A solution of **8** (*e.g.*, **8–8**) in benzene quickly absorbed CO₂ with precipitation of supramolecular material **9** (Fig. 6). This is a colorless solid, soluble in chlorinated solvents and insoluble in aromatic solvents. The chains in **9** are held together by the calixarene hydrogen bonds and carbamate CH₂N⁺H₃–O[–]C(O)NHCH₂ salt bridges. Formation of the carbamate bridges was confirmed by ¹H, COSY and ¹³C NMR spectroscopy. In the ¹H NMR spectrum of **8** in DMSO-*d*₆, the terminal –CH₂NH₂ protons were seen as a triplet at 2.53 ppm. In the salt **10**, which is formed upon dissolution and dissociation of polymer **9** in DMSO-*d*₆, these split into two 1 : 1 sets –CH₂N⁺H₃–O[–]C(O)NHCH₂–: a triplet at 2.58 ppm and a multiplet at 2.9 ppm. A broad carbamate NH signal was detected at 6 ppm. A resonance at 160 ppm in the ¹³C NMR spectrum of **10** unambiguously identified the carbamic (HN–C(O)O) carbon atom. Noteworthy, when amine **8** was treated with large excess of CO₂ in DMSO-*d*₆, the corresponding free carbamic acid formed. With the dimerization constant $K_D \geq 10^6 \text{ M}^{-1}$ for each calixarene capsule, the average degree of polymerization (further DP) of at least 10² can be theoretically estimated for chains **9** in the NMR concentration range.¹¹

Material **9** exhibits unique properties. It assembles and dissociates in a two-fashion way—upon changing either the solvent polarity or temperature. The calixarene capsules completely dissociate in DMSO, so only carbamate salt **10** can be detected (Fig. 7C). Salt **10**, most probably, undergoes further solvolysis, generating loose ion pairs, and/or equilibrates with the corresponding carbamic acid. The carbamate C–N bonds are not broken under these conditions. However,

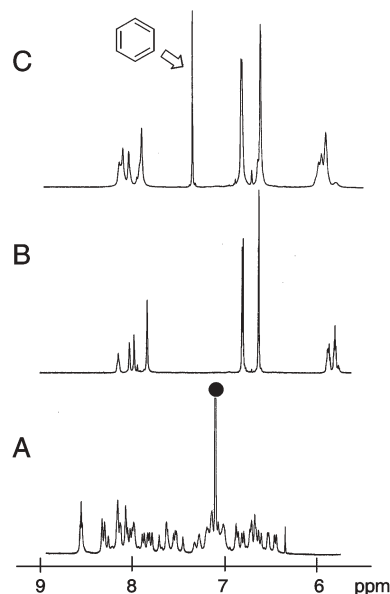


Fig. 7 Downfield fragments of ¹H NMR spectra of: (A) capsule **8–8** in C₆D₆; (B) calixarene amine **8** in DMSO-*d*₆; (C) salt **10**, prepared upon dissociation of polymer **9** in DMSO-*d*₆. For this experiment, **9** was obtained upon bubbling CO₂ through a benzene solution of **8** thus entrapping benzene. The benzene signal is assigned by an arrow. The residual solvent signals are marked as “●”.²⁴

they can be dismantled upon heating at 80–100 °C, thus releasing CO₂. As the result, in apolar solution monomeric capsules **8–8** form, and in DMSO free amine **8** is regenerated. Carbamate polymer **9** can be reconstructed simply by reintroducing CO₂.

Another interesting feature of material **9** is the multiple calixarene capsules. These are already preformed in apolar solutions. In the CO₂-initiated polymerization they trap guest molecules and transport them to the solid state. In a typical test, polymer **9**, which was obtained from benzene and dried

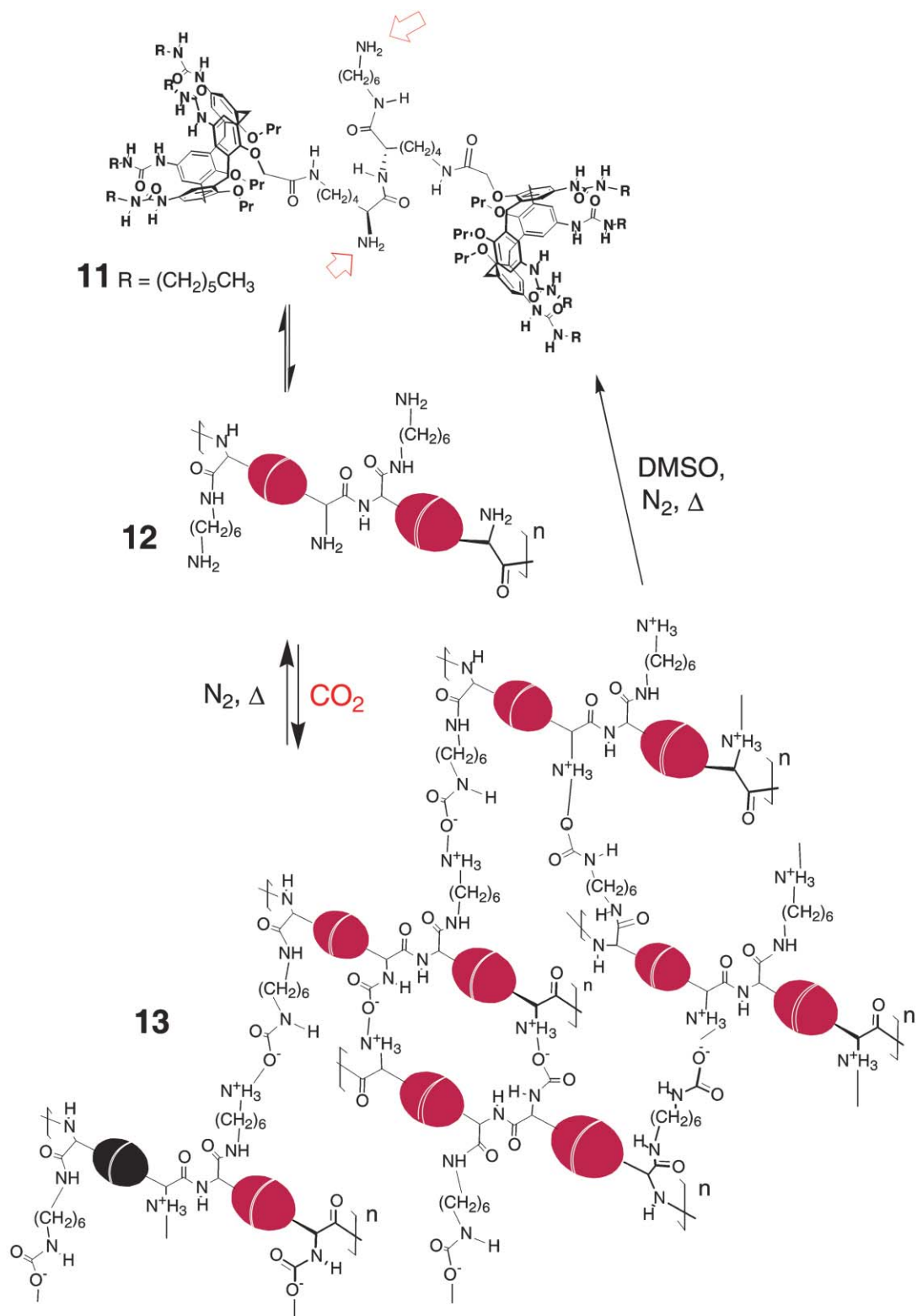


Fig. 8 Formation of cross-linked supramolecular polymer **13** includes self-assembly of polymeric chains **12** and their reaction with CO₂.

in vacuo, did not release benzene when the capsules were intact. In a suspension of **9** in non-competitive *p*-xylene, no trace of benzene was detected, but when DMSO was applied, polymeric capsules **9** broke and released visible quantities of benzene—approximately one per capsule (NMR, Fig. 7C).²⁴ More useful guests are now being tested, such as dyes and some biologically active compounds. These studies lead to *guest storing materials*.

A second generation supramolecular polymer based on carbamate chemistry is represented in Fig. 8. This is a 3D molecular network, which employ CO₂ as a cross-linking agent.¹¹

In derivative **11** two calixarene tetraurea moieties are linked with a dipeptide, a di-L-lysine chain. Calixarenes were attached to the ε-NH₂ ends, so the dilysine module orients them away from each other, in roughly opposite directions.²⁹ Such an arrangement also prevents the intramolecular assembly. A hexamethyleneamine chain was then attached to the carboxylic side of the dipeptide. Its amino group and the α-NH₂ group of **11** react with CO₂, providing cross-linking.

Similar to **8**, multiple sets of NH urea signals were seen in the ¹H NMR spectra of biscalixarene **11** in CDCl₃ and C₆D₆. These were characteristically shifted down field ($\Delta\delta \geq 2$ ppm), implying that self-assembling polymeric chain **12** formed (Fig. 8). Viscosity studies of solutions **11** in apolar solvents further confirmed the formation of polymer **12**. Thus, concentrating CHCl₃ solutions of **11** from 5 to just 40 mM

leads to a ≥ 5 -fold increase in viscosity. This was not observed for the model, non-polymeric calixarene tetraurea precursors. Solutions of **11** are viscous already at the NMR concentrations and have to be diluted for further operations. From the specific viscosity (η_{sp}) measurements, the DP value for linear chains **12** of $\sim 2.8 \times 10^2$ was estimated at 20 mM, which corresponds to the average molar mass of $\sim 7.6 \times 10^5$ g mol⁻¹.¹¹

Bubbling CO₂ through a solution of **11** in CHCl₃ or benzene yields cross-linked material **13**, which is clearly a gel (Fig. 8). The main chains in **13** are held together by a hydrogen bonding assembly of capsules, and multiple carbamate –N⁺H₃–O⁻C(O)NH– bridges cross-link these chains. This is a three-dimensional network, since the side amine groups are oriented in all three directions. Moreover, structure **13** possesses two types of amino groups, and several possibilities for the carbamate formation exist. The carbamate bridges were detected by ¹³C NMR spectroscopy. Finally, visual insight into the aggregation mode and morphology in **13** was obtained by scanning electron microscopy (SEM) of dry samples—xerogels. While the precursors show only negligible fibers formation, a three-dimensional network was obvious for **13** (see Fig. 2).¹¹

Reaction of calixarene **11** and CO₂ is special, because it converts linear supramolecular polymeric chains **12** into supramolecular, three-dimensional polymeric networks **13**. These are also switchable and can be transformed back to the linear chains **12** without breaking them. While supramolecular

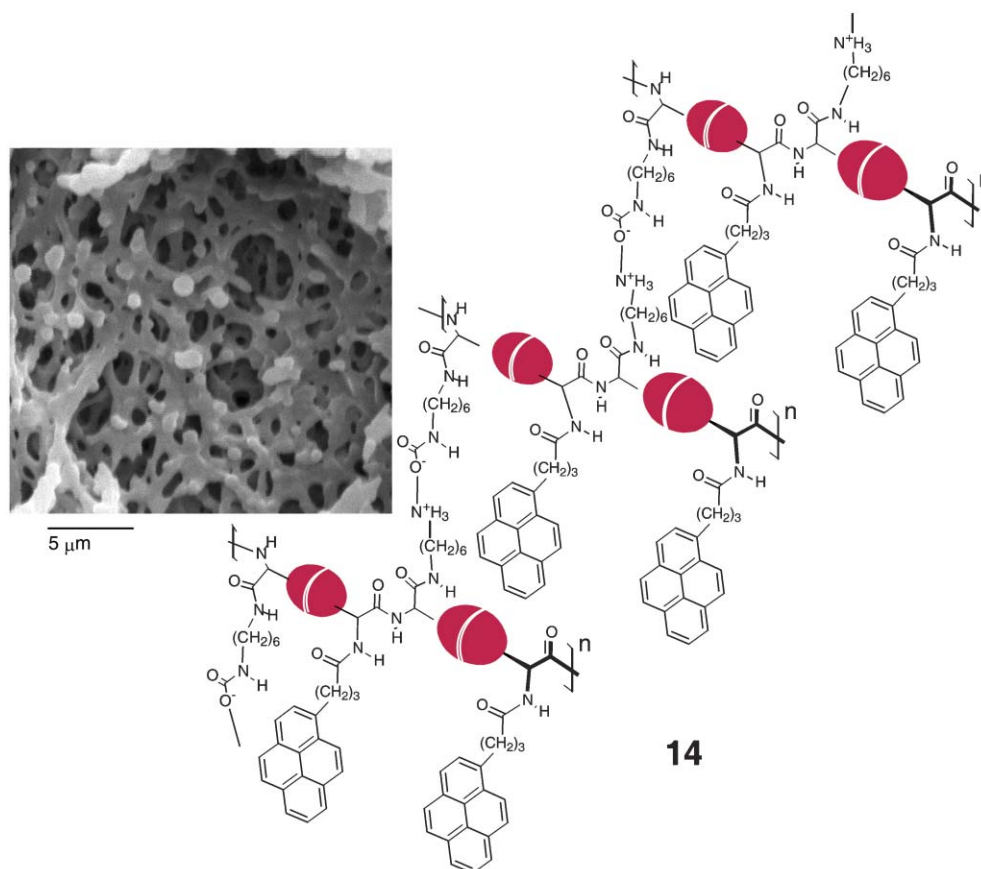


Fig. 9 Fluorescent cross-linked gel **14** and its SEM image.

cross-linked polymers are known,²³ they break upon dissociation of non-covalent aggregates, which compose them. Material **13** is different, as it only releases CO₂ and keeps hydrogen bonding intact.

Gel **14** was obtained from benzene and benzene–CHCl₃ solutions of biscalixarene **15** and CO₂ (Fig. 9 and Fig. 10).³⁰ The polymeric chains here possess multiple fluorophore units—pyrene moieties, brought together through hydrogen bonding and carbamate bridges. Accordingly, material **14** is fluorescent and may act as a vehicle for energy migration. The aggregation degree and therefore the fluorophore local concentrations can be controlled and switched on–off, as described earlier. Formation of the carbamate bridges in **14** was routinely confirmed by ¹³C NMR spectroscopy. As previously described, they can be broken after heating solution **14** for 1 h at ~100 °C and bubbling N₂ through it. The SEM pictures of the corresponding xerogels revealed, in particular, well-defined pores of ~1–3 μm diameter, which can be used for guest/solvent entrapment (Fig. 9).

In the preliminary photophysical experiments, we noticed a striking contrast in fluorescent behavior of xerogel **14**, obtained from benzene and benzene–nitrobenzene, 95 : 5 solutions of derivative **15** (Fig. 10).³⁰ The former is strongly fluorescent (λ_{ex} = 347 nm), but the latter is not. Nitrobenzene is known to quench fluorescence of pyrene.³¹ Incorporated within the gel's pores, molecules of nitrobenzene appear in

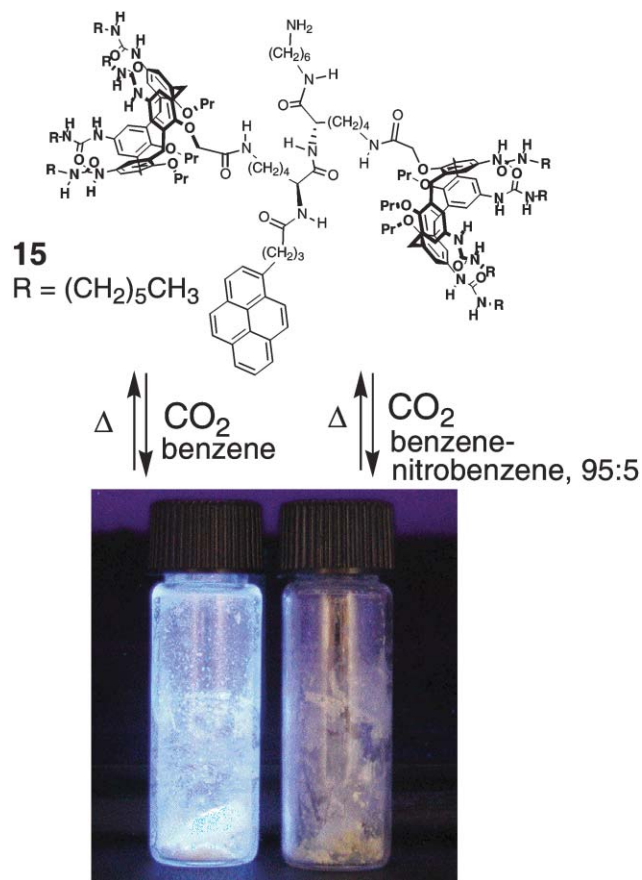


Fig. 10 Gels **14**, obtained from benzene and benzene–nitrobenzene, 95 : 5 solutions of derivative **15** have strikingly different fluorescent properties.

close proximity to the multiple pyrene donors, and energy transfer effectively occurs. In another experiment, dropwise addition of nitrobenzene (up to 10% v/v) to the benzene suspension of fluorescent xerogel **14**, 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

The development of novel methods of chemical sensing, fixation and utilization of CO₂ are clearly of great interest, and supramolecular chemistry may help. In addition to the described approaches, other avenues are also being explored. One of them is designing CO₂-philic molecules and structural fragments, whose attachment to chelating agents, surfactants, catalysts and other ligands would enhance the solubility of such compounds in scCO₂.³² Carbonyl derivatives may be useful for these purposes. Spectroscopic techniques and computations have recently identified interesting Lewis acid–base complexes between CO₂ and carbonyl containing compounds, including polymeric ones—esters, *cis*-amides and some others.^{33,34} These studies also help to understand interactions between CO₂ and membrane polymers.

Another interesting direction is encapsulation of CO₂. It has been known for decades, that CO₂ (and also a variety of other gases) can be encapsulated within self-assembled (H₂O)_{*n*} lattices in the solid state.³⁵ Hydrogen-bonded inclusion complexes of water are called clathrate hydrates. Recently hydrates of CO₂ were found in ocean bottoms. In principle, CO₂ can be buried in the deep ocean in order to reduce the release of this greenhouse component to the atmosphere. Among organic molecular containers, α-cyclodextrin effectively traps CO₂ in water. The corresponding clathrate complex in this case was isolated simply by the precipitation.³⁶ Cram's hemicarcerands also encapsulated CO₂, both in solution and in the solid state.^{37,38} Atwood and co-workers recently demonstrated that *p*-*tert*-butylcalix[4]arene crystals rapidly and selectively absorbed CO₂ from a CO₂–H₂ mixture, leaving the H₂ behind.³⁹ These findings can be used for purification of H₂. Decamethylcucurbit[5]uril—a smaller relative of cucurbituril—was found to entrap a variety of lipophilic gases, including CO₂, both in aqueous solution and the solid state.⁴⁰ By circulating air through the powder of this compound, a 5% level of CO₂ was decreased to 0.01%. Very recently, CO₂ was trapped inside single-walled carbon nanotubes.⁴¹ These and other studies imply that cavity-containing solids for CO₂ entrapment, storage and release are of great interest.

As for carbamate chemistry, CO₂ can now be optically detected and also used to build switchable, supramolecular polymeric materials and gels. Incorporation of other functionalities within dynamic three-dimensional carbamate networks is being explored, such as capsules, ionophores, catalytic sites, polymerizable groups for covalent cross-linking, *etc.* Given the high diversity of supramolecular approaches, the capabilities here are really beyond limits. Supramolecular chemistry and technology are also being applied for sensing and conversion of other important gases.¹²

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