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Progress in Supramolecular Chemistry of Gases

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The current progress in molecular recognition and supramolecular chemistry of gases is presented. The structure and properties of supramolecular gas-receptor complexes is discussed. Novel chromophoric and fluorophoric sensors for detection of gases are introduced. Studies on molecules and materials for gas entrapment, separation, storage and release that involve synthetic containers, capsules and nanotubes are overviewed. It is shown that supramolecular fixation of gases leads to stable and selective chemical reagents. Gases can also be used as building blocks. Polymers and reversible, dynamic nanostructures from gases are presented. Their potential application as storing and separating materials is discussed.

Introduction

Molecular chemistry is based on covalent bonds. Noncovalent forces define supramolecular chemistry.[1] Three years ago, we introduced supramolecular chemistry of gases as an emerging research field.[2] Gases compose the atmosphere and play important roles in medicine, science, technology and agriculture. Extensive circulation of gases necessitates the development of novel methods of their detection and monitoring. Another important issue is their storage and chemical fixation. Applying principles and techniques of supramolecular chemistry and molecular recognition for these purposes has successfully began.

Gases are small molecules, with no many sites for interactions, if any, and their chemistry is relatively limited. An individual approach and higher degree of design is required to make effective receptors for gases. Often, a combination of different binding forces is necessary. Despite significant experimental difficulties, chemists learned how to handle gases at the times of alchemistry and, further, pneumatic chemistry.[3] In fact, early experiments on gas complexation started already two hundred ago. Stable clathrate hydrates of gases were discovered in the 1820s, but it took another century before first X-ray crystallographic studies were performed.[4] Gas encapsulation in organic hosts, naturally occurring cyclodextrins, were published in the 1950s.[5] Then came gas-binding heme proteins. Already from the early X-ray crystallographic studies of dioxygen complexes of hemes it became clear that, in addition to the iron–gas interactions, hydrogen bonding, cavity effects and solvation should be taken into account.[6] A wide variety of successful heme models were then prepared, based on sterically hindered, or "superstructured", metalloporphyrins. Metal–gas interactions have been utilized in gas sensors and catalysis. In the 1980s, synthetic molecular containers, hemicarcerands and cryptophanes, were introduced that reversibly trapped common gases.[7,8]

These early developments in molecular recognition of gases had led to their supramolecular chemistry, which, in addition to the selective complexation, broadly covers gas chemosensors, molecular containers and materials for gas entrapment, storage and release, supramolecular reactivity and catalysis, self-assembling nanostructures and materials

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from gases, and, lately, the reversible, dynamic covalent chemistry of gases. In this review, the up-to-date progress report on supramolecular chemistry of gases will be presented. The most recent works from our laboratory and others will be discussed, reflecting accomplishments in the field. We will show that this field has now matured enough to hold a respectful place in the supramolecular science.

Supramolecular Sensing of Gases

Utilizing traditional supramolecular approaches to detecting ions and neutral molecules has led to novel sensors for gases. For example, molecules have been designed and synthesized that are functionalized with fluorophore and chromophore groups. Upon interaction with gases, these directly report on their presence through easily detectable spectral changes and/or even visually. Importantly, the sensor design is not limited by any particular structure, because the dyes do not directly react with the gas but rather serve as reporters.

Introducing CO_2 gas to a solution of 1-(aminomethyl)-pyrene (**1**, Figure 1) in polar aprotic solvents, such as DMSO or DMF, results in significant (>10 times) increase in the fluorescence emission (λ_{em} = 408 nm, λ_{ex} = 341 nm).[9] The species responsible for the observed blue fluorescence is the free carbamic acid **2**. Carbamic acids are still very rare. Itself, the amine **1** only weakly emits fluorescence under ambient conditions, which is due to the photo-induced electron transfer (PET) quenching of the excited fluorophore by a lone pair of the intramolecular amino group. In the carbamic acid **2**, the 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. Bubbling N_2 through solutions of **2** or simply heating (60–80 °C) results in the loss of fluorescence. Under these conditions, CO_2 is released and the free amine **1** is regenerated. Similar behavior was recently documented for a number of fluorescent primary amines.[10]

A recently introduced potential sensor for SO_2 involves an indicator-displacement assay (Figure 1).[11] While indicator-displacement assays are widely used for sensing of ions, this is the first example for gases. It is well documented that SO_2 and secondary or tertiary amines form stable charge-transfer complexes, both in solution and in the solid state. When amines were added to (tetraphenylporphyrin)-Zn (**3**) in $CHCl_3$, the solution changed from red to dark-green. A bathochromic shift of $\Delta\lambda$ ca. 10 nm was observed for the Soret band, indicating the formation of **3**·amine complexes. After this, SO_2 gas was introduced, and the original red color was restored. The Soret band returned to its position for the free porphyrin **3**. The **3**·amine complexes dissociated, and new SO_2·amine adducts formed. The porphyrin **3** thus served as an indirect colorimetric indicator for SO_2. The system discriminates between SO_2 and such typical exhaust gases as CO_x, NO_x and H_2O. While there are obvious UV changes simply upon addition of SO_2 to an amine, incorporating the porphyrin in the assay brings the response into the visible region of the spectrum. There is a possibility to modify both amines and porphyrins to achieve more colorful responses, and also to detect SO_2 in aqueous solutions and at the gas-solid interface.[11]

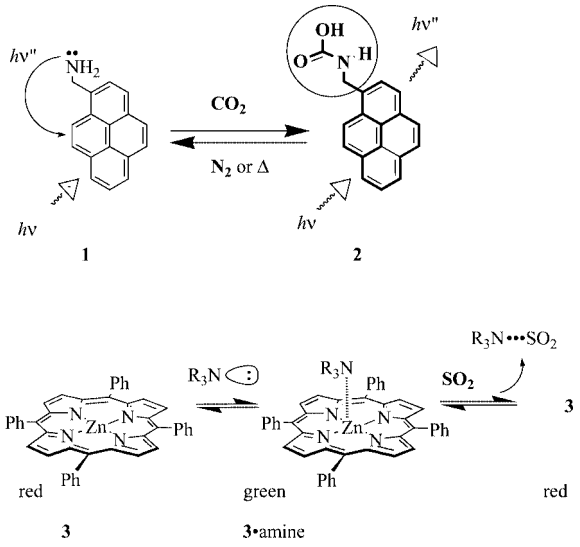

Figure 1. Sensing of CO_2 and SO_2 is based on reversible interactions.

Attempts to detect NO_x gases have been made. Kochi and co-workers showed that when converted into the cation radical, the calix[4]arene **4** strongly complexes NO with the formation of the deep-purple calix-nitrosonium species **5** (Figure 2).[12] In these, the NO molecule is transformed into nitrosonium cation (NO^+). Strong charge-transfer interactions between NO^+ and the π-surface of **4** places the guest molecule between the cofacial aromatic rings at a distance 2.4 Å, which is shorter than the typical van der Waals contacts. A value for the association constant $K_{assoc} > 5 \times 10^8$ M^{-1} was estimated in CH_2Cl_2. Similar complexes were also obtained for calix[4]arenes in other conformations.

We studied host–guest complexes formed upon reversible reaction between NO_2 and calix[4]arenes.[13] NO_2 is a paramagnetic gas of an intense brown-orange color. It exists in equilibrium with its dimer N_2O_4, which is colorless. The dynamic interconversion between NO_2 and N_2O_4 makes it impossible to study either of these species alone. N_2O_4 may disproportionate to ionic $NO^+NO_3^-$ while interacting with simple aromatic derivatives. We found that tetrakis-*O*-alkylated calix[4]arenes in their *cone* and *1,3-alternate* conformations react with NO_2/N_2O_4 to form stable nitrosonium complexes, for example **6** (Figure 2). These complexes are deeply colored as well. They are strong ($K_{assoc} >> 10^6$ M^{-1}) but dissociate upon addition of water or alcohols. More stable calixarene-nitrosonium complexes were isolated upon addition of Lewis acids such as $SnCl_4$ and BF_3–Et_2O.

The visible absorption spectrum of complex **6** showed broad charge-transfer band at λ_{max} ca. 560 nm (ε =

8×10^3 M^{-1} cm^{-1}). While neither calixarenes nor NO_2 absorb in this region, addition of as little as ca. 1 equiv. NO_2 to the solution of **6** in chlorinated solvent results in appearance of the charge-transfer band. Calix[4]arenes can detect NO_2 at micromolar concentrations.[14] Interestingly, wider calix[5]-, calix[6]- and calix[8]arenes do not encapsulate NO^+ and no color was detected upon exposure to NO_2.

We also discovered a novel reaction between NO_2/N_2O_4 and Ru^{II} porphyrins which might be useful for the gas sensing.[15] Reaction of 2 equiv. NO_2 with [(carbonyl)(tetra-*p*-tolylporphyrin)Ru^{II}] [Ru(TTP)(CO) (**7**)] in CH_2Cl_2 results in a rapid, quantitative formation of nitrosyl nitrato [Ru(TTP)(NO)(ONO_2)] (**8**) (Figure 3). The orange solution of **7** turned dark-green upon addition of NO_2. In the IR spectrum of **8** (in KBr), the carbonyl ν_{CO} band at 1950 cm^{-1} is replaced by a new, very strong nitrosyl band ν_{NO} at 1852 cm^{-1}. Upon mixing with NO_2/N_2O_4, the Soret band at λ_{max} = 412 nm decreased in its intensity, while the Q-

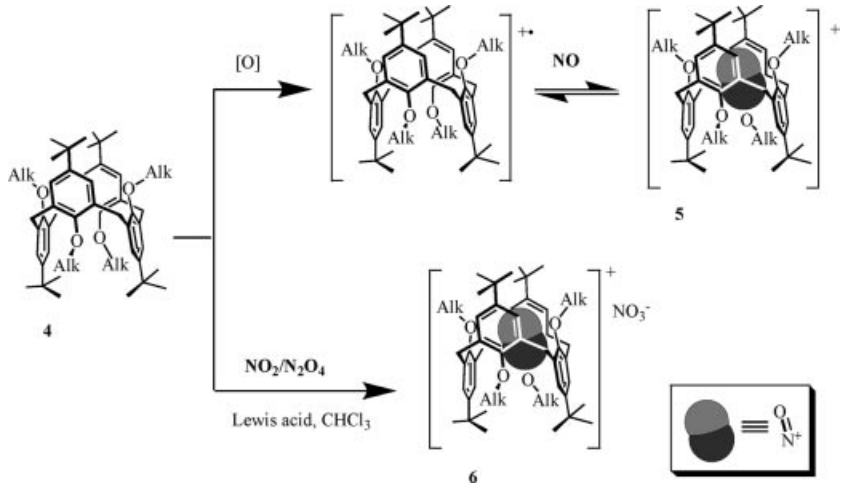

Figure 2. Encapsulation complexes of NO_x gases with calix[4]arenes. Formation of calixarene-NO^+ complexes.

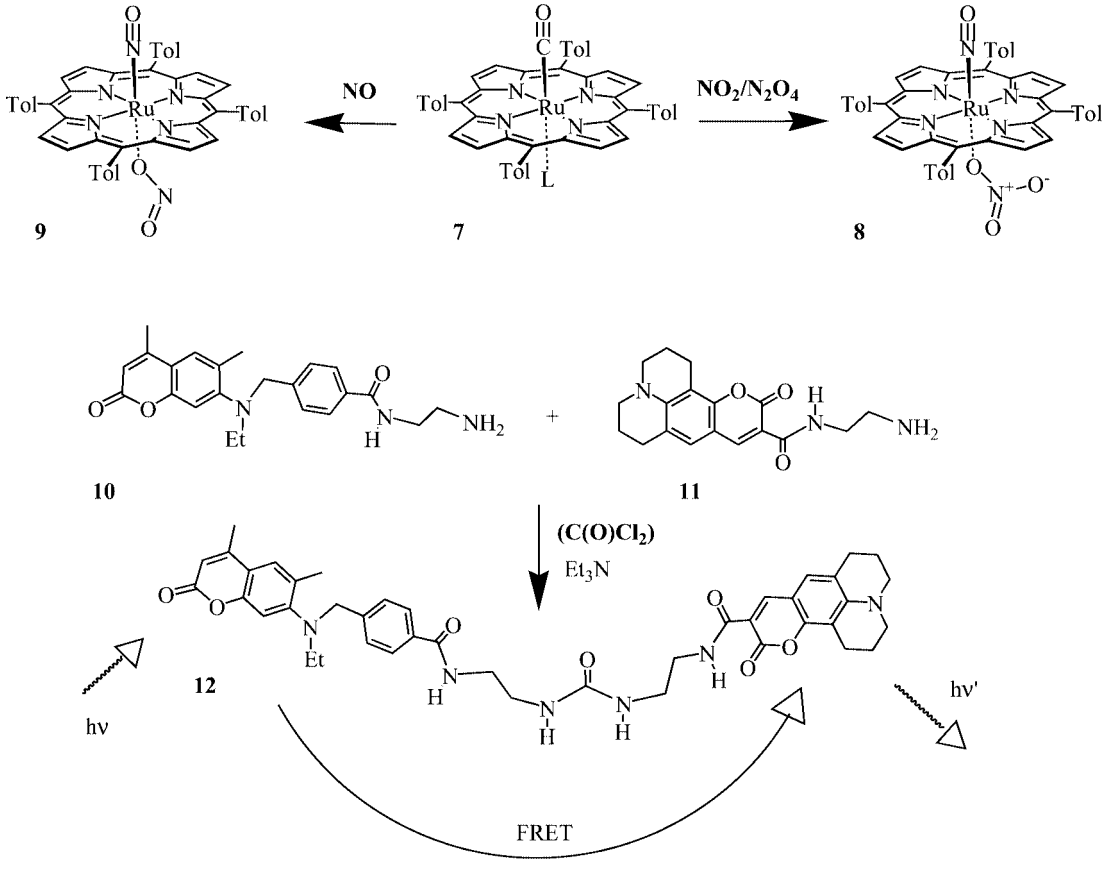

Figure 3. Optical sensors for NO_x gases and phosgene.

band at λ_{max} = 528 nm disappeared and a new band at λ_{max} = 564 nm emerged. The rapid color changes upon exposure of the porphyrin **7** to NO_2/N_2O_4, both in solution and in the thin film, could be conveniently utilized for the gas sensing. When treated with NO gas in CH_2Cl_2, [Ru(TTP)(CO)] (**7**) transformed into the nitrosyl nitrito [Ru(TTP)(NO)-(ONO)] porphyrin **9**, whose appearance and spectral features are different from those of **8**.[16]

We recently introduced potential phosgene sensors based on fluorescence resonance energy transfer (FRET).[17] It includes a selective chemical reaction between phosgene [$C(O)Cl_2$] and donor and acceptor fluorophores, which bring them together, within the appropriate Förster distance. Phosgene serves here as a cross-linking agent. When the emission spectrum of the donor overlaps with the absorption spectrum of the acceptor, FRET occurs upon irradiation of the donor and strong emission of the acceptor can be detected. This reports on the presence of phosgene. There is a renewed interest in the development of phosgene sensors due to the increased threat of weapons deployment by terrorists.

When donor and acceptor coumarins **10** and **11** are mixed together with triphosgene (as a phosgene simulant) in the presence of Et_3N in $CHCl_3$, the hybrid urea **12** forms (Figure 3). At concentrations as low as $\leq 10^{-5}$ M, the donor excitation at λ = 343 nm leads to the acceptor emission at λ = 464 nm. In a control experiment only utilizing acceptor coumarin **11**, no emission in this region was detected under these conditions. This implies a FRET phenomenon in urea **12**. In addition, the fluorescence from the donor unit at λ = 424 nm decreased. This is due to the quenching, indicating that efficient energy transfer took place from the donor to the acceptor. The response of compounds **10** and **11** to triphosgene can be conveniently followed even with the naked eye. The detection limit is ca. 5×10^{-5} M. The systems is selective, because other gases rarely serve as cross-linking agents.

Encapsulation of Gases and New Materials

Molecular Containers

Already in the 1950s it was discovered that α-cyclodextrin interacted with Cl_2, Kr, Xe, O_2, CO_2, C_2H_4, CH_4, C_2H_6, C_3H_8, and n-C_4H_{10} in water, under elevated pressures, with the formation of stable clathrates.[5] Synthetic molecular containers brought new features, because their encapsulation abilities could be tuned through the synthesis. Thus, prepared in the early 1990s by Cram hemicarcerand **13** reversibly encapsulated O_2, N_2, CO_2, and Xe already at 1 atm (Figure 4).[18] Due to the sterically restricted approach to the cavity, the exchange between the free and occupied **13** was slow on the NMR time-scale. Recently we discovered that He, N_2, N_2O, and CO_2 could be encapsulated and stored by hemicarcerand **13** even in the solid state.[19] For example, upon flushing the powder containing **13** and **13**·N_2 with CO_2 or N_2O, hemicarceplexes **13**·CO_2 or **13**·N_2O were quantitatively obtained. Being similar to the exchange in solution, these findings open the whole new area on gas encapsulation at the gas-solid interface.

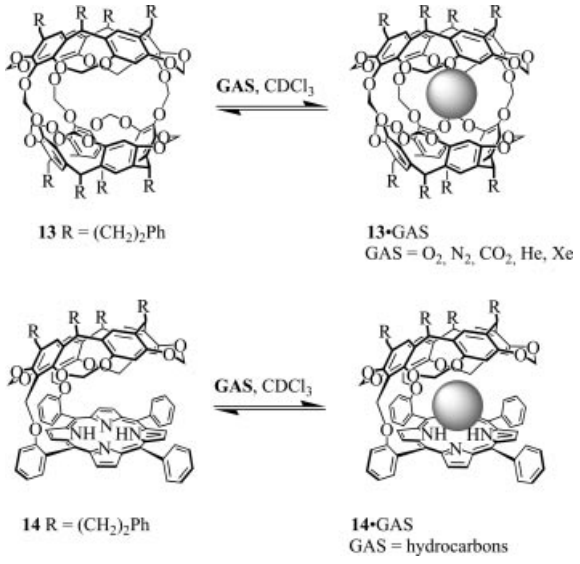

Figure 4. Reversible encapsulation of gases in hemicarcerands.

Naruta and co-workers demonstrated reversible encapsulation of hydrocarbons into the hemicarcerand **14** (Figure 4).[20] The exchange between the free and complexed gases in $CDCl_3$ was slow on the NMR time-scale, so the complexes were kinetically stable. Methane, ethane, propane, cyclopropane, ethylene and acetylene were trapped and the K_{assoc} values were between 10 (ethane, cyclopropane) and 130 M^{-1} (acetylene). The presence of a porphyrin fragment in **14** allowed for the metal insertion. In the future, it should be possible to synthesize catalytic hemicarcerands for hydrocarbon gases based on this approach.

So-called cryptophane-A **15** readily encapsulated CH_4 (K_{assoc} = 130 M^{-1}) and especially Xe (K_{assoc} = 3000 M^{-1}) in $(CDCl_2)_2$ (Figure 5).[21] The latter atom is highly polarizable, but inert and hydrophobic. The NMR parameters of the ^{129}Xe (I = 1/2, natural abundance 26%) isotope are very sensitive to the environment. Pines and Wemmer utilized these features to develop a biosensor for targeting biomolecules in solution.[22] Their typical xenon biosensor **16** consisted of a cryptophane-A cage attached to a biotinylated peptide through a linker (Figure 5). When this biosensor was titrated with its biomolecular target, the avidin protein, its ^{129}Xe NMR signals shifted. Spatial resolution of a specific target protein in vitro at micromolar concentration was demonstrated. The inherent spectral information of these chemical shift imaging techniques makes this approach suitable for multiple analysis, where a number of different biosensors with unique Xe chemical shifts bind to different targets.

Progress has also been made with self-assembling capsules. Such capsules usually form through reversible noncovalent interactions between two concave subunits. In the

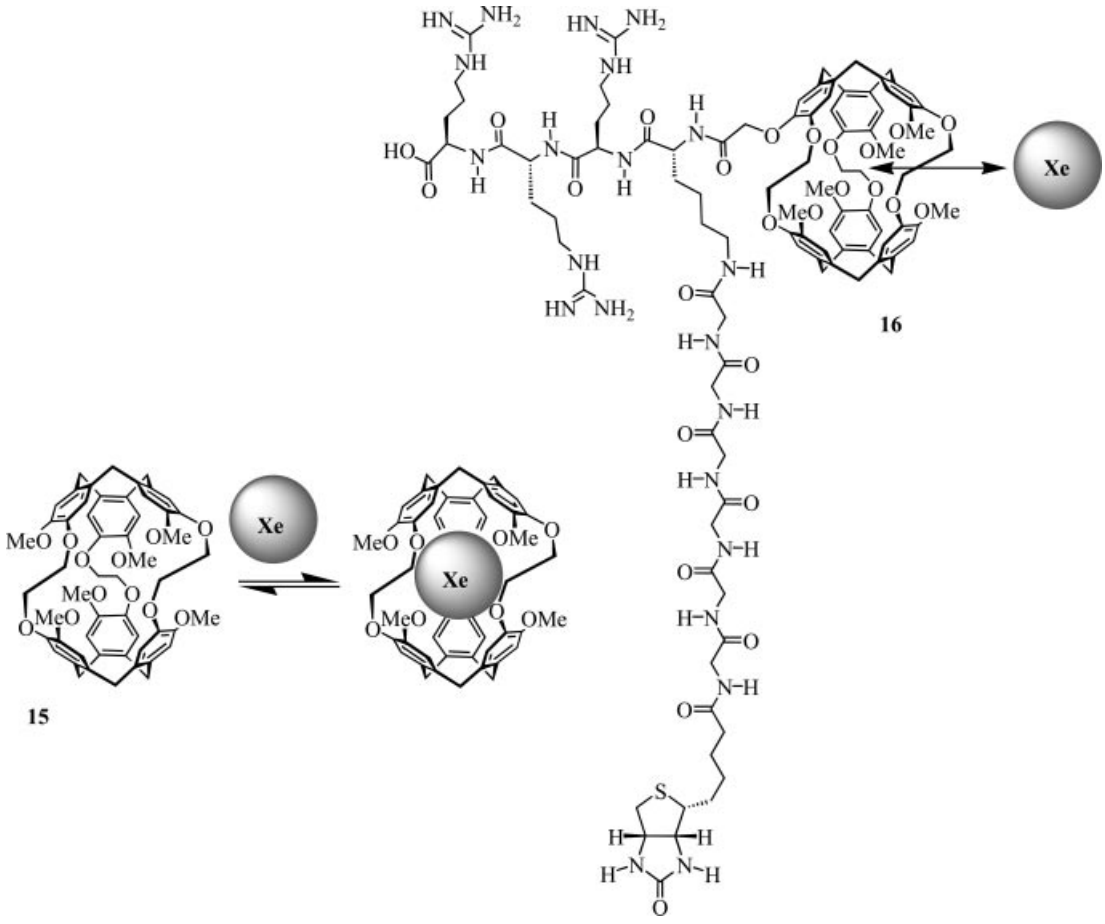

Figure 5. Encapsulation of Xe by cryptophane-A may be used for biomedical imaging.

early studies, Rebek showed that "tennis balls" assembled through hydrogen bonding around a molecule of CH_4, ethylene, or Xe in $CDCl_3$ solution.[23,2] Novel phenomena have emerged with larger self-assembling structures. Binary co-encapsulation of ethane, cyclopropane, and isomeric butanes together with larger organic guest (*p*-xylene, naphthalene and anthracene) was observed for nanoscale cylindrical capsule **17** (Figure 6).[24] Noteworthy, these gases alone could not be trapped. Gaseous hydrocarbons were encapsulated in aqueous solution by a self-assembled dimer of deep cavitand **18**.[25] In fact, the gases served as templates for such self-assembly (Figure 6). Two molecules of *n*-butane were trapped directly from the gas phase and the preference of butane over propane was observed. These studies open new doors for natural gas purification and separation through encapsulation.

For many applications, the drawback of noncovalent complexes with gases lies in their relatively low thermodynamic stability. An alternative approach is based on reversible chemical transformation of gases upon complexation. In this case, they produce reactive intermediates with higher affinities for the receptor molecules. This approach may result in conceptually novel sensors and materials and also offers attractive opportunities in the design of chemical reagents from gases. In this review, chemical transformation of gases upon complexation will be demonstrated for NO_2/N_2O_4, as well as CO_2 and SO_2.

We already reported that calix[4]arenes, for example **4** (Figure 2), interact with NO_2/N_2O_4 and entrap NO^+ species within their interiors.[13,14] NO^+ is generated upon disproportionation of N_2O_4 to $NO^+NO_3^-$. Due to the charge transfer between NO^+ and π-electron-rich calixarene tunnel, very strong ($K_{assoc} >> 10^6$ M^{-1}, $\Delta G^{295} >> 8$ kcal/mol) complexes **6** form. These can be used for sensing of NO_x gases. At the same time, the calixarene-NO^+ complex **6** and its analogs can release NO^+ and serve as nitrosating agents.

Nitrosation is important in preparative organic chemistry. Synthetic alkyl nitrites, nitrosamines, nitrosamides, and nitrosothiols are widely used in medicine as NO-releasing drugs. In total synthesis and methodology, –N=O serves as an important activating group, allowing easy transformations of amides to carboxylic acids and their derivatives. In addition, nitrosation mimics interactions between biological tissues and NO_x gases.

Chemical properties of the encapsulated NO^+ were controlled by the cavity and were different from those in bulk solution.[26] The calixarene-NO^+ complexes were quite stable towards moisture and oxygen, and could be handled, for days, without a dry box and/or an N_2 atmosphere. On the other hand, they were decomposed within few minutes

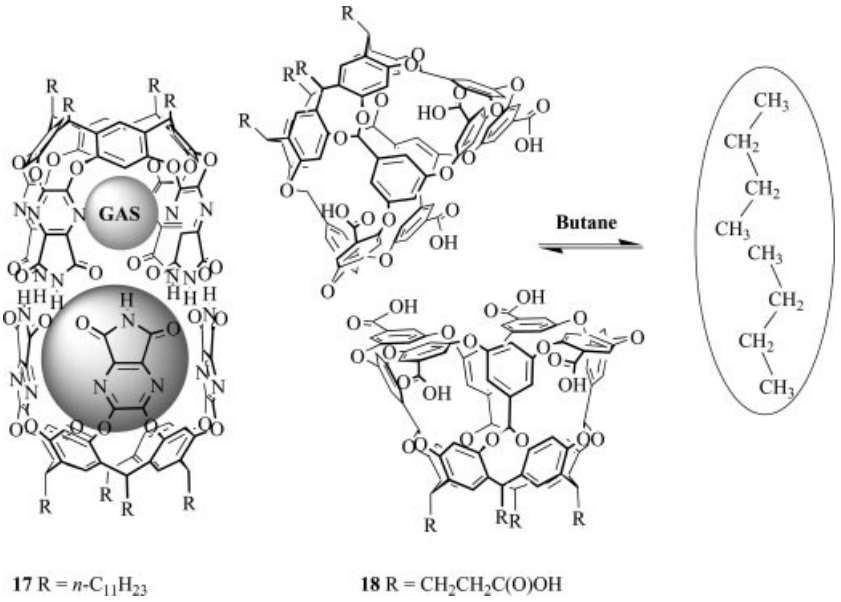

Figure 6. Self-assembling capsules for gas entrapment.

by addition of larger quantities of H_2O or alcohols, regenerating the free calixarenes.

The secondary amide substrates R′C(O)NHR (**19**) reacted with calixarene-NO^+ complex **6** with remarkable selectivity.[26] When mixed with the equimolar solution of **19** in $CHCl_3$, complex **6** reacted quickly at room temperature, yielding up to 95% of the *N*-nitrosamides **20** (Figure 7). Dark-blue solutions of **6** lost their color upon addition of the substrates, which is a visual test for the reaction. Among the variety of amides **19**, only those possessing *N*-Me substituents were transformed to the corresponding *N*-nitrosamides **20**. No reaction occurred for substrates with bulkier groups. The calixarene cavity was obviously responsible for such delicate size-shape selectivity. Larger substrates simply could not reach the encapsulated NO^+.

Polymer-supported nitrosating reagents were also prepared.[14,26] Among the advantages of such reagents are the ease of their separation from the reaction mixture, their recyclability, and the simplification of handling toxic NO_x gases. Particularly useful are soluble polymers, as they overcome problems associated with the heterogeneous nature of the reaction conditions. A variety of polymers are commercially available, but NO_2/N_2O_4 react with many of them, causing destruction and aging. Accordingly, robust and stable polyethylene glycol (PEG) and silica gel were employed.

The deep-purple PEG-supported material **21**·$(NO^+)_n$ was obtained upon simply bubbling NO_2/N_2O_4 through the solution of polymer **21** in CH_2Cl_2 for several minutes, followed by brief flushing with N_2 to remove the remaining NO_2/N_2O_4 gases (Figure 7).[14] Material **21**·$(NO^+)_n$ effectively nitrosated amides **19** in homogenious CH_2Cl_2 and the preference for less bulky *N*-Me amides **19** was observed. After the reaction, material **21** was simply precipitated with hexanes and filtered. The dark-blue silica gel **22**·$(NO^+)_n$ was prepared by bubbling NO_2/N_2O_4 through the suspension of **22** in CH_2Cl_2, followed by filtration and washing with CH_2Cl_2 (Figure 7).[26] Material **22**·$(NO^+)_n$ is quite robust

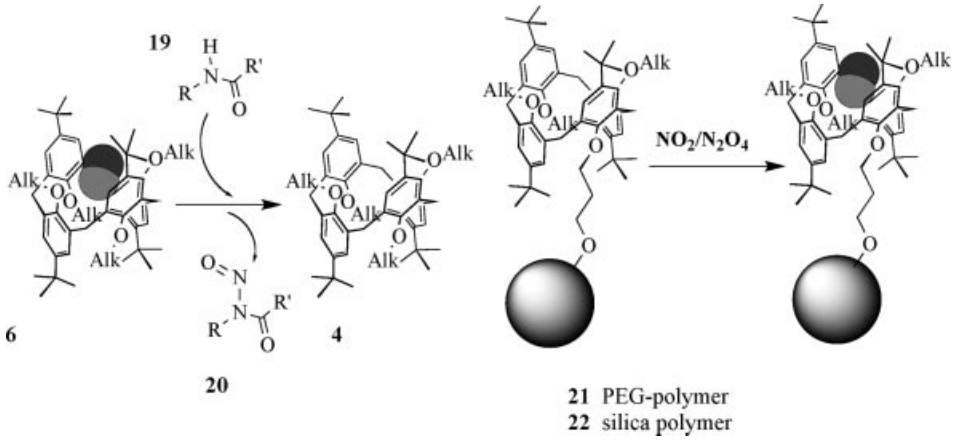

Figure 7. Nitrosating reagents and materials based on calixarenes and NO_x gases.

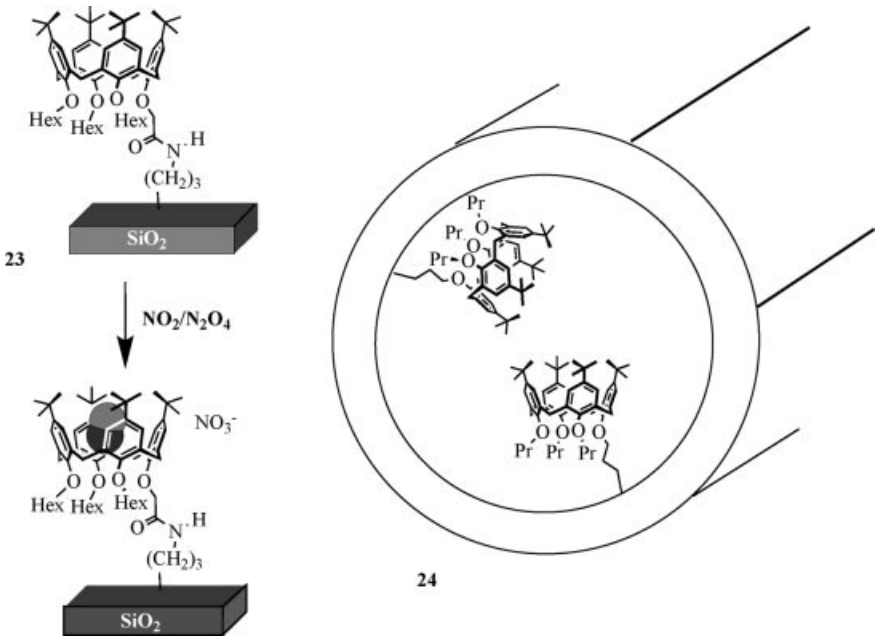

Figure 8. Calixarene based materals for NO_x entrapmet and storage.

and does not change the color for several days. For nitrosation, it was suspended in dry CH_2Cl_2, equimolar amount of amides **19** was then added, and the reaction mixture was stirred at room temperature for 24 h. The reactant's color disappeared, thus indicating the reaction progress, and material **22** was separated by simple filtration. The size-shape selectivity, observed for the solution experiments with complexes **6**, was clearly seen in this case as well. The yields of nitrosamides **20** with less hindered *N*-Me fragments were obtained up to 30%, while bulkier *N*-Et and *N*-Pr derivatives **20** formed in much smaller quantities ($\leq$8%). In control experiments, involving starting silica gel, no visible amounts of **20** were seen, again emphasizing the role of calixarene cavity in the described reactions. Tight but reversible encapsulation of NO^+ species by calix[4]arene monomers and materials based on them thus offers size-shape selectivities, previously unknown for conventional nitrosating agents.

On the basis of these findings, calixarene materials were synthesized for entrapment of NO_x gases (Figure 8). Specifically, the calix-silica gel **23**[13] and calix[4]arene-based periodic mesoporous silica **24**[27] were prepared. In the NO_2 entrapment experiments, a stream of the gas was passed through columns loaded with the materials **23** and **24**, instantly producing a dark purple color, indicative of NO^+ complexation. The complexation was also confirmed by IR spectroscopy, where the characteristic calixarene-NO^+ stretch was observed at $\tilde{\nu}$ ca. 1920 cm^{-1}. The solid-supported complexes were stable for hours, especially for mesoporous silica material **24**.[27] In this case, the NO^+ entrapment was also detected by elemental analysis. The materials can be regenerated by simply washing with alcohol and reused.

Fullerenes and Carbon Nanotubes

With current interests in fabricating nanoscale structures, much attention is focused on fullerenes and nanotubes. In early studies, fullerene C_{60} **25** was shown to permanently trap Noble gases upon heating to 650 °C and 2000–3000 atm pressures (Figure 9).[28] Even under these, rather extreme conditions, Noble gases were incorporated with the fractional levels of only 0.1%. It was proposed that the gas molecule enters C_{60} through a window formed by the reversible breaking of one or more carbon–carbon bonds. Ac-

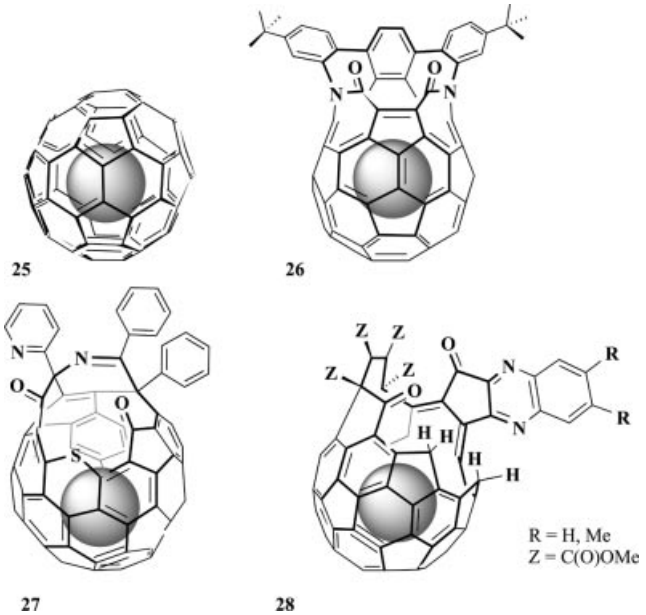

Figure 9. Simple and modified fullerenes effectively complex gases.

cordingly, the theoretical barriers for such processes were very high (≥ 200 kcal/mol). In reverse, the encapsulated gases can be released by breaking the carbon–carbon bonds upon heating under vacuum.

Alternatively, fullerenes can be opened through so-called molecular surgery. Studies with synthetically opened fullerenes require heavy synthetic efforts and may still be rather far from commercial applications. At the same time, the findings are impressive. Open-neck C_{60} based bislactam **26** encapsulated gases much more easily than **25** (Figure 9).[29] With the distance between parallel rings in the orifice of 4.1 Å, calculated insertion barriers for He and H_2 are 24.5 and 41.4 kcal/mol, respectively. Experimentally, ^{3}He gas was inserted into **26** at 475 atm and 300 °C over 7.5 h (1.5% maximal yield). For H_2, it took 100 atm, 400 °C and 48 h (5% yield). With the even larger orifice (3.75 × 5.64 Å), fullerene **27** quantitatively encapsulated H_2 at 200 °C and 800 atm (Figure 9).[30] The encapsulated H_2 molecule was detected by ^{1}H NMR (–7.25 ppm in *o*-[D_4]dichlorobenzene) and also MALDI-TOF mass spectrometry. The experimental activation energy for the H_2 escape is 34 kcal/mol. Spectacularly, a single H_2 molecule encapsulated inside **27** was recently observed by a single-crystal X-ray diffraction analysis.[31] Moreover, the orifice in complex **27**·H_2 can be closed via a four-step synthetic procedure, resulting in completely sealed **25**·H_2.[32] This complex is as stable as C_{60} itself.

Much faster guest exchanges were observed for fullerenes with even larger openings. Derivative **28** possesses 20-membered orifice of 4.2 x 6.5 Å and was found to easily trap an H_2O molecule (Figure 9).[33] In the ^{1}H NMR spectrum of **28**·H_2O, a sharp singlet at δ = –11.4 ppm in [D_2]tetrachloroethane was detected for the encapsulated guest. This however disappeared upon addition of D_2O, indicating rather frequent guest mobility. The H_2O molecule can also be replaced by CO under 9 MPa.[34] The encapsulated CO molecule was identified through ESI mass spectrometry, ^{13}C NMR and IR spectroscopy. For example, in the ^{13}C NMR spectrum of **28**·CO in $CDCl_3$, a sharp signal for the gas was observed at δ = 174 ppm. The chemical shift of free CO gas in $CDCl_3$ is 185 ppm. When placed in $CDCl_3$ with some H_2O at 40 °C, complex **28**·CO releases its guest within two days, leaving the mixture of free fullerene **28** and **28**·H_2O.

Some industrially and biologically important gases can be stored inside single-walled carbon nanotubes (SWNTs).[35] Typical SWNTs diameters range from 7 to 20 Å. Initial synthesis of SWNTs often produces sealed structures, which prevents the gas adsorption within the interiors. Chemical treatments, for example, oxidation, lead to open-ended SWNTs. There have been only limited experimental examples published on the interior entrapment of gases by SWNTs. Among them are He, N_2, O_2, H_2O, NO, CO_2, I_2 and CF_4.[35,36]

Synthetic Nanotubes

Synthetic analogs of SWNTs have recently been introduced (Figure 10). These are based on calix[4]arenes and reversibly interact with NO_2/N_2O_4.[37,38] In nanotubes **29**–**32**, *1,3-alternate* calix[4]arenes are rigidly connected from both sides of their rims with pairs of diethylene glycol linkers. In this conformation, two pairs of phenolic oxygen atoms are oriented in opposite directions, providing diverse means to modularly enhance the tube length. The synthesis is based on a straightforward, modular strategy, which incorporates reliable Williamson-type alkylations and provides yields as high as 80%. The nanotubes possess defined inner tunnels of 6 Å in diameter and may entrap multiple NO^+, one per each cavity. On the other hand, they can be emptied at will, in a nondestructive manner. With lengths up to 5 nm and with up to five guests entrapped, these nanotubes are the largest synthetic molecular containers known to date. For example, tubes **31** and **32** are 35 and 45 Å long, respectively. They are of ca. 2.3 and 2.8 kDa in molecular weight.

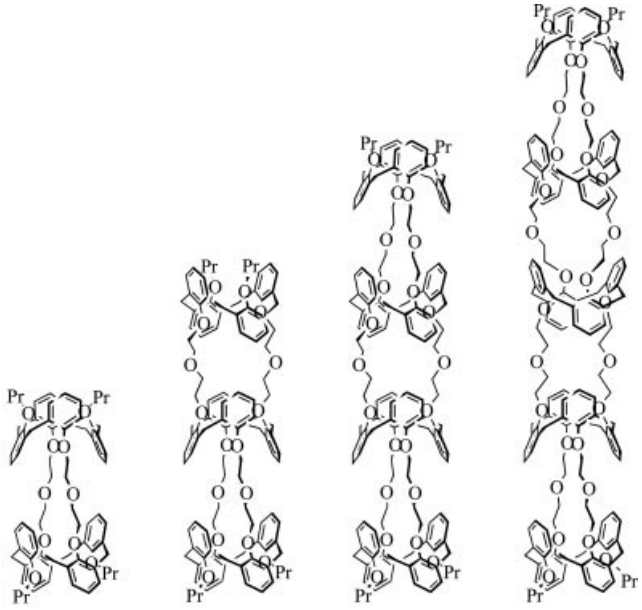

Figure 10. Synthetic nanotubes for NO_x gases.

Exposure of **29**–**32** to NO_2/N_2O_4 in chlorinated solvents results in the rapid encapsulation of NO^+ cations within its interior. The guest position inside **29**–**32** can be deduced from FTIR and NMR analysis. The characteristic purple color implies that the NO^+ guests are entrapped inside. The charge-transfer bands responsible for this are observed at λ_{max} ca. 550 nm. The NO^+ entrapment process is reversible, and addition of water quickly regenerated the empty tubes.

In the solid state, longer nanotube units **30** pack head-to-tail, in straight rows, resulting in infinitely long cylinders (Figure 11).[37] The neighboring nanocylinders aligned parallel to each other. In each nanocylinder, molecules **30** are twisted by 90^O relative to each other, and the Ar–O–Pr propyl groups effectively occupy the voids between the adjacent molecules. In such an arrangement, the intermolecular dis-

tance between two neighboring tubes in the nanocylinder is ca. 6 Å. The nanocylinders are separated from each other by ca. 9 Å. This supramolecular order comes with the tube length and is without precedent for conventional, shorter calixarenes. The unique linear nanostructures maximize their intermolecular van der Waals interactions in the crystal through the overall shape simplification. Such a unique arrangement resembles that of SWNTs bundling.

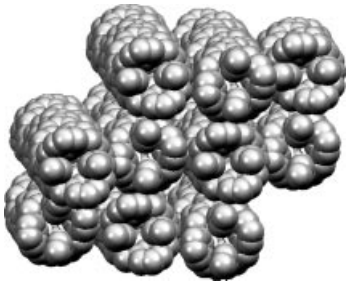

Figure 11. Solid-state packing of calixarene nanotubes (X-ray).

Among possible applications of these synthetic nanotubes are nanowires and also optical sensors for NO_x. Chemical fixation of NO_x is also of great interest. The tubes can be used for molecular storage of active nitrosonium and act as size-shape selective nitrosating reagents. Generation of NO gas inside and its release is also possible. Finally, in contrast to other molecular containers,[7] supramolecular chemistry of synthetic nanotubes is still not well explored.

Solid Networks and Materials

That certain porous solids form inclusion complexes with smaller molecules has been known for years, but with recent developments in materials chemistry and nanotechnology, this field has expanded. Among clathrates, gas hydrates are probably most known. Hydrogen-bonded inclusion complexes of water are called clathrate hydrates.[4] In gas clathrate hydrates, voids are much larger than in ice, and the nets are unstable unless occupied. Cages formed by water crystals under ambient temperatures (<300 K) and moderate pressures (>6 atm) may accommodate CH_4 and other gaseous hydrocarbons, fluorinated and chlorinated hydrocarbons and their hybrids, CO_2, N_2, N_2O, SO_2, H_2S, H_2Se, O_2, Xe, Ar, and Kr. Recently hydrates of CH_4 and CO_2 became of the growing interest. CO_2 can be buried as a hydrate in the deep ocean in order to reduce the release of this greenhouse component to atmosphere. Hydrates of CH_4 can serve as a source of hydrocarbons and, in general, organic carbon. Literature on other various clathrates with gases is also available.[39]

Extensive studies are being undertaken in the search for stable nano- or microporous networks utilizing coordination polymers. Porosity of these polymers can be programmed depending on the applications. A variety of metal-organic microporous materials (MOMs) and frameworks (MOFs) have been designed for gas storage and transport.[40] MOMs and MOFs were found to adsorb N_2, O_2, Ar, CO_2, N_2O, H_2, CH_4, and acetylene. The remarkable ability of certain MOFs in sorption of H_2 makes them attractive candidates for vehicular hydrogen-based economy. The U. S. Department of Energy's ambitious 2010 target for storage of H_2 is 6 wt.-%, and it should be 9 wt.-% by 2015. Up to date however, the storage capacities of MOFs are not sufficiently high for practical applications. The best results have been achieved so far are within 3 wt.-%.[41]

Much less effort has been devoted to assessment of pure organic solids as gas sorbents, in which building blocks are linked by covalent bonds. Organic molecules typically adhere to close-packing principles and do not afford porous structures. Calix[4]arenes offer a remarkable exception. We found that He, N_2, N_2O, and CO_2 could be encapsulated and stored by hemicarcerand **13** in the solid state.[19] Atwood and co-workers showed that CH_4, CF_4, C_2F_6, CF_3Br and other low-boiling halogenated alkanes could be reversibly entrapped and retained within the lattice voids of a crystalline calix[4]arene framework.[42] Such gas-storing crystals appeared to be extremely stable and release their guests only at elevated temperatures, several hundreds of °C above their boiling points. Ripmeester further discovered that calix[4]arene cavities in such crystals are directly involved in the gas complexation.[43] The Atwood's team further demonstrated that calix[4]arene dimerizes in a crystalline phase into a hourglass-shaped cavity, capable of gas entrapment.[44] These crystals soak up gases when stored in air. Absorption of CO_2 was particularly rapid, but CO, N_2, and O_2 were also trapped. Of special importance, the calixarene crystals selectively absorbed CO_2 from a CO_2/H_2 mixture, leaving the H_2 behind. This phenomenon can be used for purification of H_2. Very recently, Atwood showed that calix[4]arene crystals can also absorb H_2, CH_4, acetylene, and NO_x gases.[45,46] Cavity-containing solid materials for gas entrapment, storage and release have thus emerged.

Very recently covalent organic framework (COF) **33** was designed and synthesized.[47] Material **33** is composed of expanded porous graphitic layers, with pore sizes up to 27 Å. COF **33** is thermally stable till 500–600 °C and have a great surface area of 1590 m^2/g. This exceeds the highest reported surface area of 1300 m^2/g for macroporous ordered silica.

Polymer with intrinsic microporosity (PIM) **34** have recently been prepared, which contains preformed bowl-shaped cyclotricatechylene cavities (Figure 12).[48] This material has surface area of 830 m^2/g and adsorbs 1.4 wt.-% H_2 (at 1 bar, 77 K). In the future, it will be important to construct PIMs with much larger accessible surface areas (> 2000 m^2/g) and maintain an ultramicroporous structure to retain maximal interactions between the walls and H_2. For this, calixarene cavities should be of great interest.

Ripmeester showed that H_2 storing capacities of clathrate hydrates could be increased to 4 wt.-% by simply adding THF.[49] Prior to this study, the pressure required to maintain the stability of clathrate hydrates with H_2 was very high (≈2 kbar). The pressure can now be decreased to 100 bar by simply co-occluding THF molecules in the clath-

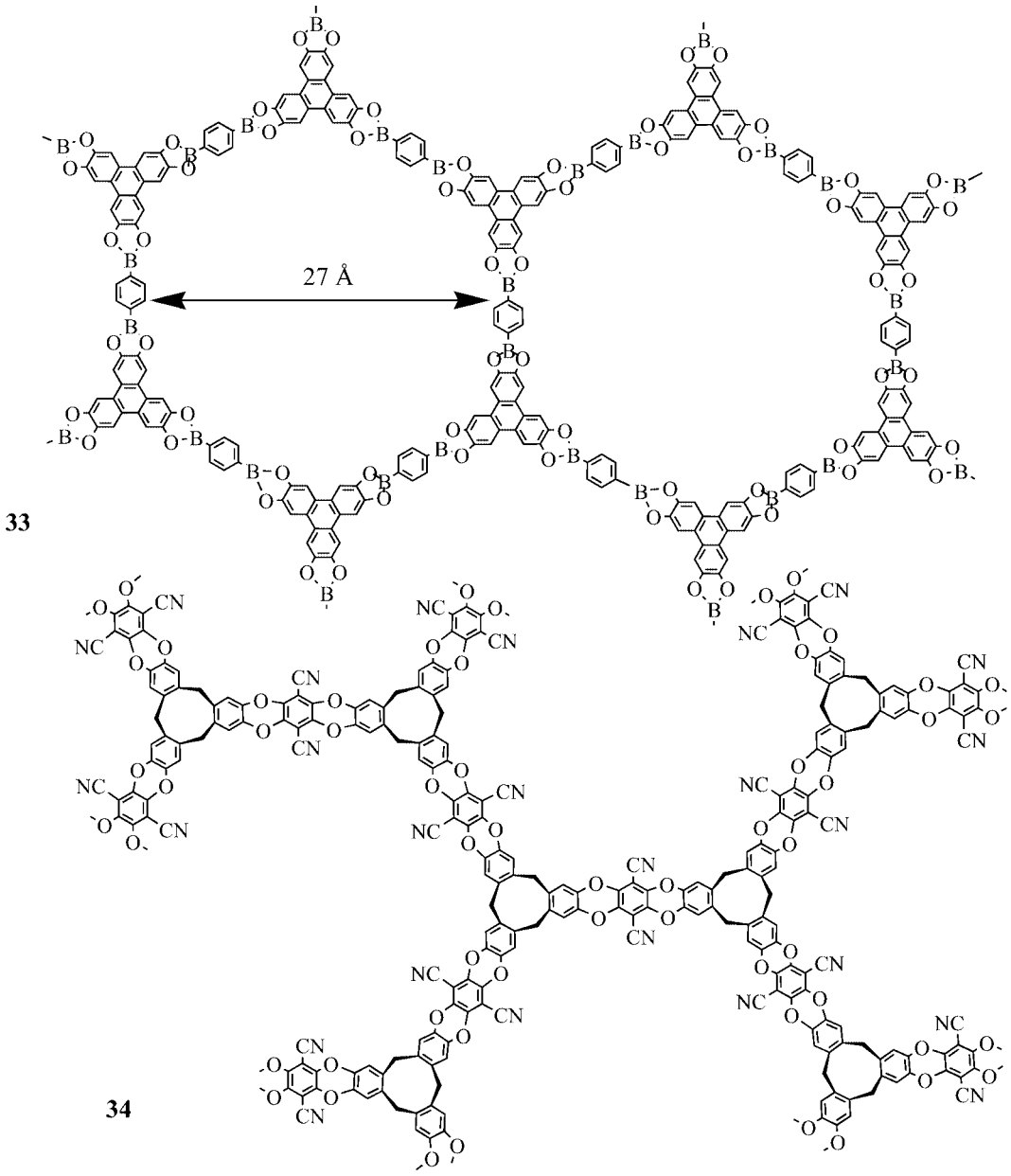

Figure 12. Porous organic materials (COF and PIM) for gas entrapment, separation and storage.

rate. While the system's hydrogen capacity still falls short of the Department of Energy requirement, it offers some advantages. For instance, the storage materials – water and THF – are cheap, and the environmental and health hazards are relatively low.

Materials from Gases

Gases can be used as building blocks for polymers and materials. We recently discovered a convenient, one-step procedure for the preparation of diaryl sulfamides **35** directly from SO_2 gas.[50] SO_2 was activated through the formation of donor-acceptor, noncovalent complexes with amine bases such as Py and Et_3N. An excess of SO_2 along with I_2 and Py or Et_3N in MeCN smoothly converts primary arylamines into *N*,*N*′-diarylsulfamides in up to 85% yield (Figure 13). The amine base forms known donor-acceptor complexes, such as $Py{\cdot}I^+I^-$ and further $Py{\cdot}I^+I_3^-$ with I_2 and $Py^+{\cdot}SO_2^-$ with SO_2. These complexes further lead to iodosulfinate (SO_2I^-) and still elusive sulfuryl iodide (SO_2I_2), which then successively reacts with $ArNH_2$, producing $ArNHSO_2I$ and then $ArNHSO_2NHAr$. The developed protocol was applied for the synthesis of oligomeric sulfamide **36** from *p*-phenylenediamine (about 35% yield). In the solid state, short and oligomeric sulfamides yield extensive networks of intermolecular N–H···O=S hydrogen bonds and thus self-assemble into soft porous materials.[50]

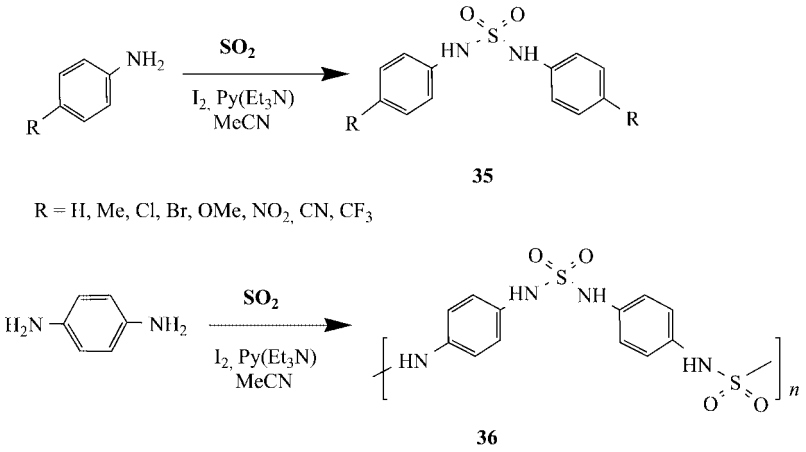

Figure 13. SO_2 is used as a building block for self-assembling sulfamide monomers and polymers.

More advanced progress has been made towards materials from CO_2.[51] It has been known for decades that CO_2 smoothly reacts with amines at ordinary conditions to yield carbamates.[9,52] At the same time, carbamates are thermally unstable and release CO_2 upon heating. Several years ago, we proposed to use this chemistry in the preparation of self-assembling, reversible polymers.[53] Reversibly formed polymers are usually called supramolecular polymers.[54] They represent a novel class of macromolecules, in which monomeric units are held together by noncovalent bonds such as hydrogen bonds, metal–ligand interactions, or van der Waals forces. Supramolecular polymers combine features of conventional polymers with properties resulting from the bonding reversibility.

Linear and cross-linked supramolecular polymers could be prepared from biologically friendly amino acid lysine and its di- and tripeptides and CO_2.[55] These peptides possess primary ε-NH_2 groups, which upon reaction with the gas form carbamate bridges at ambient temperatures in apolar organic solvents ($CHCl_3$, benzene) and even in the presence of 10% MeOH. Resulting gels were easily isolated from solution, dried and stored refrigerated for several months. At the same time, they thermally release CO_2 and convert back to the corresponding monomers. As a consequence, their structure and physical properties are switchable.

Further developments involved hydrogen bonding. Monomeric units were designed, which strongly aggregate in apolar solution and possess "CO_2-philic" primary amino groups on the periphery.[56] Calixarenes were employed as self-assembling units. Calix[4]arene tetraurea dimers are probably the most studied class of strong hydrogen bonding aggregates.[57] These dimers form in apolar solution with $K_D \geq 10^6$ M^{-1} and are held together by a seam of sixteen intermolecular C=O···H–N hydrogen bonds. This results in a rigid inner cavity of ca. 200 Å^3 which reversibly encapsulates a solvent molecule or a benzene-sized guest.

Supramolecular polymer **37** is a 3D molecular network, which employs CO_2 as a cross-linking agent (Figure 14).[56] In monomer **38**, two calixarene tetraurea moieties are linked with a dipeptide, di-L-lysine chain. Calixarenes were attached to the ε-NH_2 ends, so the dilysine module orients them away from each other, in roughly opposite directions. Such arrangement also prevents intramolecular assembly. A hexamethyleneamine chain was then attached to the carboxylic side of the dipeptide. Its amino group and the α-NH_2 group of **38** react with CO_2, providing cross-linking.

Viscosity studies of solutions **38** in apolar solvents confirmed the formation of hydrogen-bonding polymer **39**. The degree of polymerization for linear chains **39** of ca. 2.8×10^2 was estimated at 20 mM, which corresponds to the average molar mass of ca. 7.6×10^5 g/mol. Bubbling CO_2 through solution of **39** in $CHCl_3$ or benzene yields cross-linked material **37**, which is a gel. The main chains in **37** are held together by hydrogen bonding assembly of capsules, and multiple carbamate–N^+H_3···O^-C(O)NH bridges cross-link these chains. This is a three-dimensional network, because the side amine groups are oriented in all three directions. The carbamate bridges were detected by ^{13}C NMR spectroscopy. Finally, visual insight into the aggregation mode and morphology in **37** was obtained by scanning electron microscopy (SEM) of dry samples, or xerogels. While the precursors show only negligible fiber formation, a three-dimensional network was obvious for **37**.

Reaction of the calixarene **38** and CO_2 is special, because it converts linear supramolecular polymeric chains **39** into supramolecular, three-dimensional polymeric networks **37**. These are also switchable and can be transformed back to the linear chains **39** without breaking them. While supramolecular cross-linked polymers are known,[58] they break upon dissociation of the noncovalent aggregates which compose them. Material **37** is different, as it only releases CO_2 and keeps hydrogen bonding intact. At the same time, the hydrogen bonds can also dissociate if polar solvent is added.[56]

The polymer **37** can be considered an early representative of so-called double dynamers. In 2005, Lehn et al.[59] introduced double dynamers as novel, dynamic polymers, which simultaneously contain noncovalent (hydrogen bonding) and reversible, dynamic covalent bonding connections in their structures.

Supramolecular polymer **37** was employed for the entrapment and controlled release of organic guests (Fig-

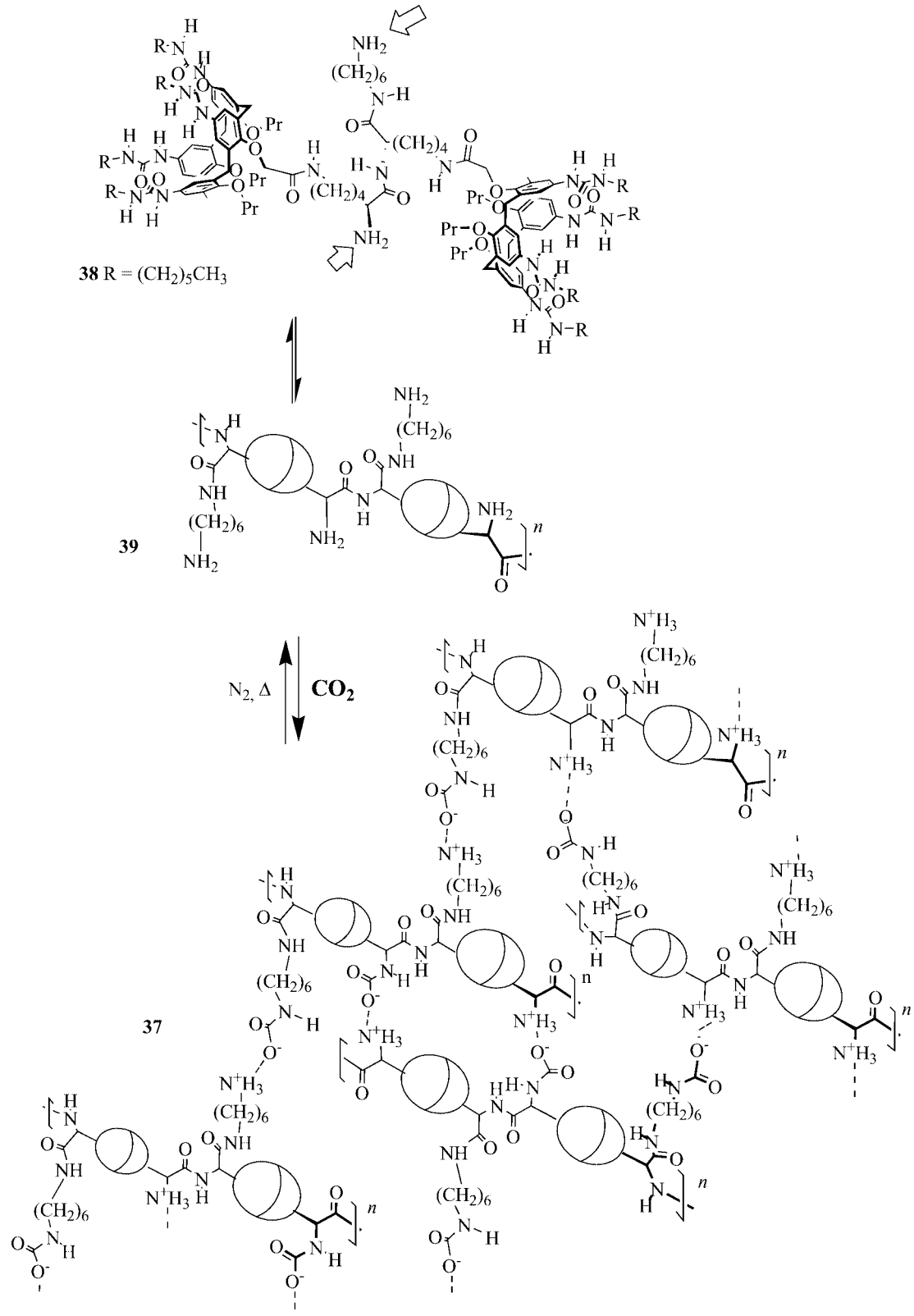

Figure 14. Supramolecular calixarene-lysine polymers can be cross-linked by CO_2.

ure 15).[60] On a molecular level, multiple voids are generated between the carbamate-lysine fragments in **37**, which are of 15–20 Å dimensions. Gel **37** was used to trap commercial dyes such as coumarins and porphyrins. Absorption spectrophotometry was employed to monitor their release. In a typical experiment, peptide **38** was dissolved in a small volume of $CHCl_3$ and then coumarin 314 or tetraphenylporphyrin were added. CO_2 was bubbled through the

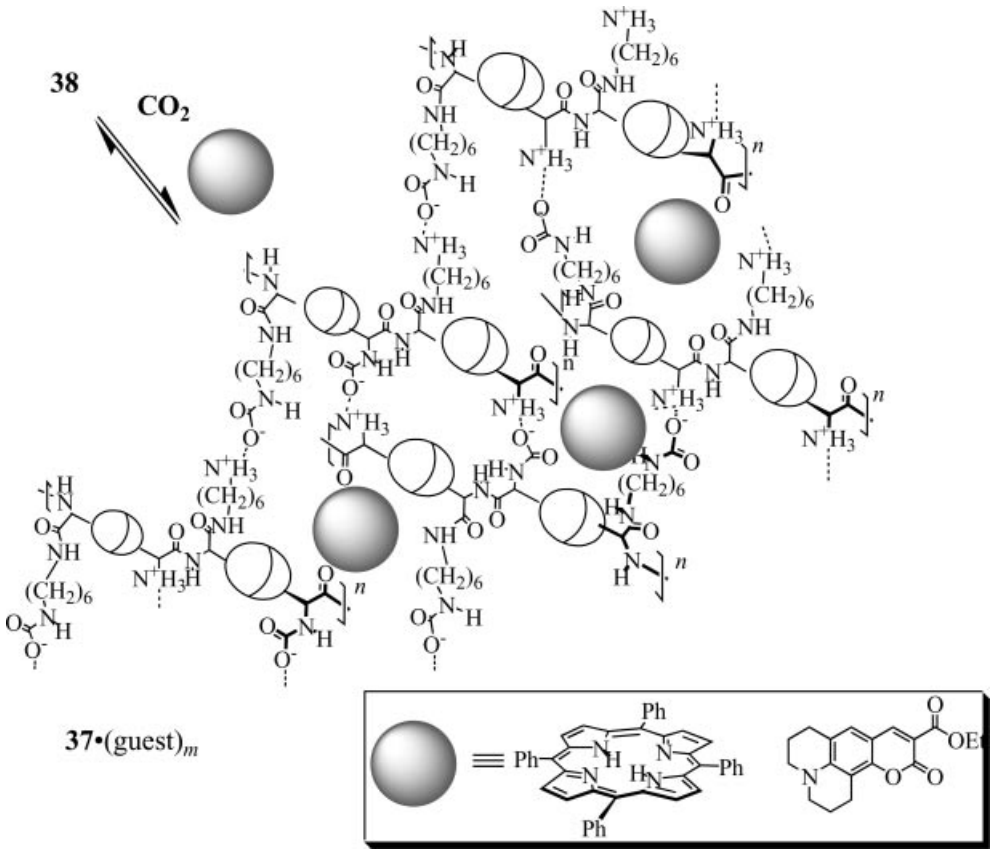

Figure 15. Guest entrapment experiments using a supramolecular, carbamate cross-linked gel.

solution for 5 min. Colored gels **37**•(guest)$_n$ were formed. The guests can be stored in dried gels indefinitely and released only upon the gel dissipation. The guests release was accomplished through changing solvent polarity (H-bond breaking) and/or temperature (CO_2 release/carbamate breaking). It was also found that lowering the pH also facilitates the CO_2 release due to the carbamate hydrolysis.[60]

The carbamate gel **40**, obtained from benzene and benzene/$CHCl_3$ solutions of the corresponding monomer **41** and CO_2, possesses multiple fluorophore units – pyrenes – brought together through hydrogen bonding and carbamate bridges (Figure 16).[61] The aggregation degree and therefore the fluorophore local concentrations can be controlled and switched on-off, as described earlier. In photophysical experiments, a striking contrast in fluorescent behavior was noticed of the xerogels **40** obtained from benzene and from 95:5 benzene/nitrobenzene solutions. The former is strongly fluorescent (λ_{ex} = 347 nm), but the latter is not. Nitrobenzene is known to quench fluorescence of pyrene. Incorporated within the gel's pores, molecules of nitrobenzene appear to be in close proximity to the multiple pyrene donors, and energy transfer is effective. In another experiment, dropwise addition of nitrobenzene (ca. 10% v/v) to the benzene suspension of the fluorescent xerogel **40**, initially obtained from benzene, resulted in the fluorescence disappearing within a few seconds. These observations could be useful in the design of switchable light harvesting materials.

Further exploring the dynamic covalent chemistry of CO_2, we discovered that this gas can be used as a building block for separating materials.[62] Separation processes are central to the chemical, materials, energy, and pharmaceutical industries. Traditional separations generally involve distillations, extractions, membrane transport processes, crystallizations and various chromatography techniques, but today molecular recognition is becoming an area of emerging importance. In our separation strategy, selective solution complexation by macrocyclic receptors is combined with the CO_2-induced molecular switching, leading to effective precipitation. Receptors can be prepared, which also possess multiple primary amino groups capable of reacting with CO_2. After complexation of target species by these receptors, CO_2 is introduced (room temp., 1 atm), which reacts with the terminal amino groups of the receptors. As the result, cross-linked carbamate polymers forms and precipitates. These polymers incorporate the target complexes within their structures. The process will thus separate the complexed species from the bulk solution and uncomplexed species. The precipitated materials can be collected and stored. On the other hand, they can release CO_2 and dissociate back to monomers upon heating or addition of acid, and subsequently release the complexed species in their pure form.

The strategy was already demonstrated using a simple, "classical" crown ether **42** and its complex with potassium

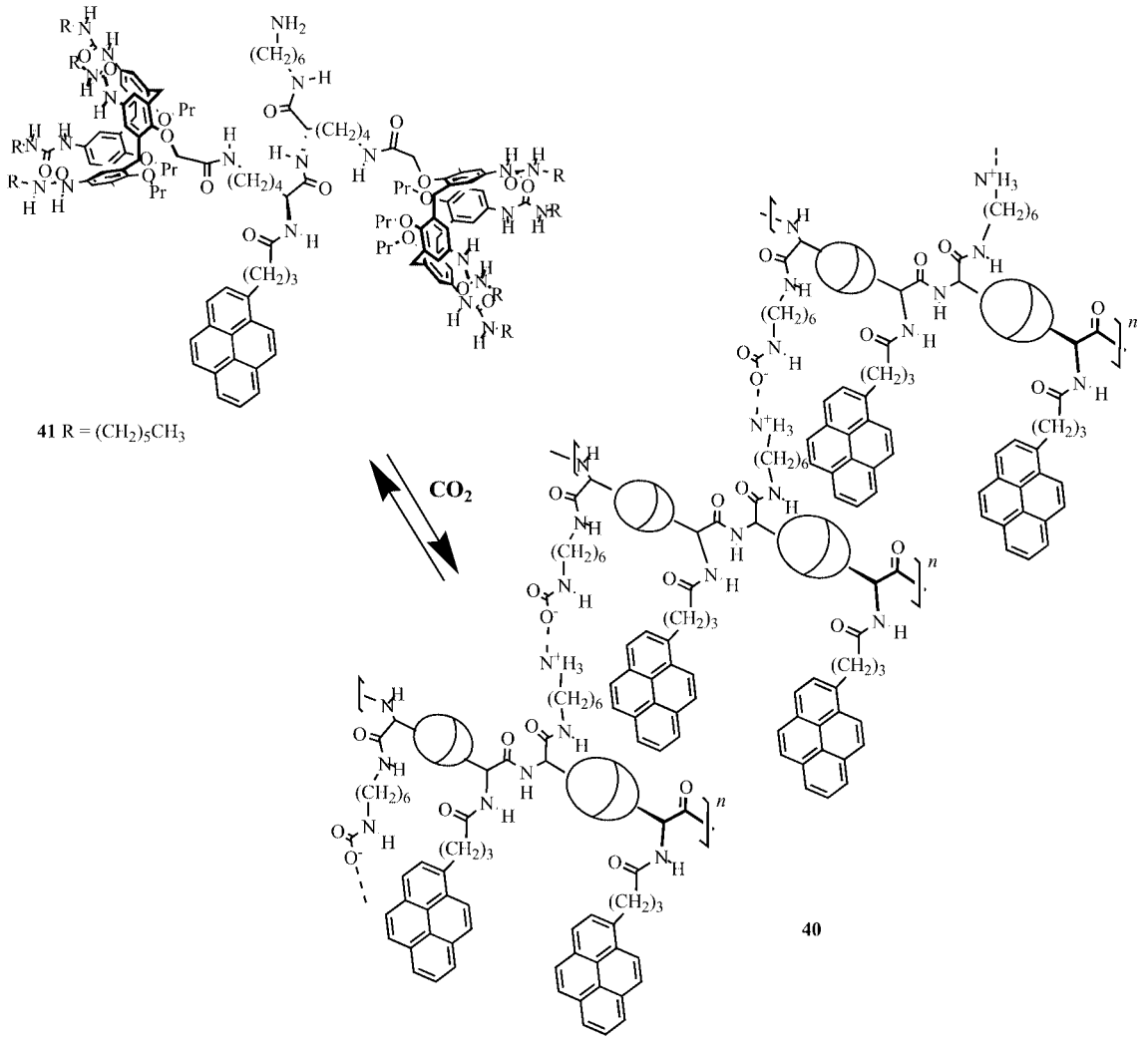

Figure 16. Fluorescent, carbamate based materials can be made using CO_2.

(Figure 17).[62] In the future, the architecture and complexation properties of the separating materials can be programmed through synthesis at the stage of their monomers. In contrast to known separating polymers and materials, which impose significant phase-transfer restrictions on complexation, the proposed receptors complex guests in

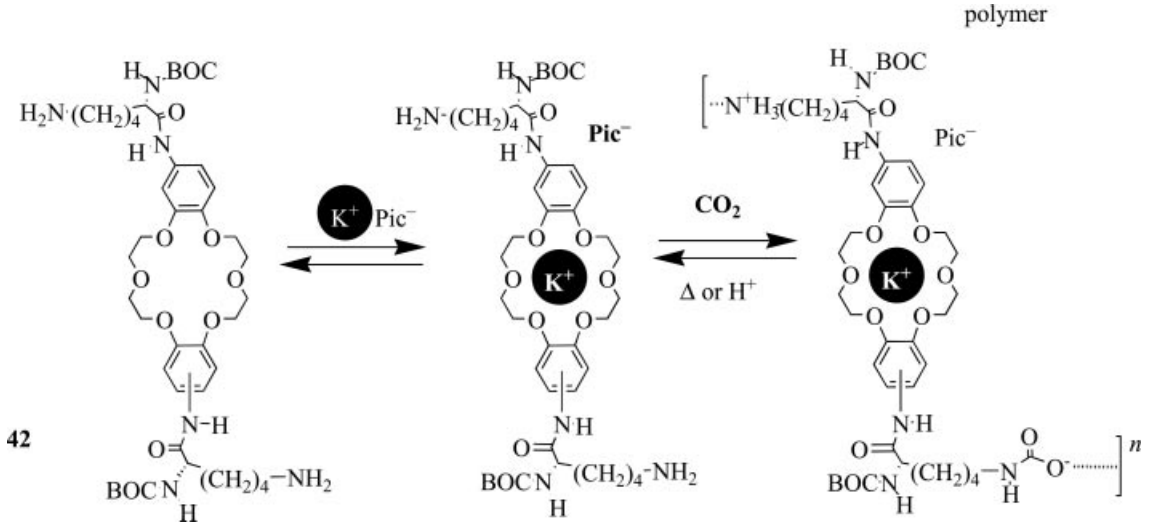

Figure 17. Novel separation strategy involving CO_2 gas.

solution, as monomers, and only polymerize upon reaction with CO_2. Due to effective precipitation, large quantities of solvent can be recovered and reused. The storage is accomplished without the use of solvent, which is also preferred.

Conclusions

The progress in supramolecular chemistry of gases over just the last several years has been spectacular. But most certainly, this is just a beginning of much bigger developments. Deeper understanding of the structure and properties of existing gas-receptor complexes should lead to novel discoveries in molecular recognition of gases. In the future, more supramolecular sensors, chromophoric and fluorophoric, for detecting and monitoring gases in the atmosphere, technology and medicine will be introduced. Supramolecular fixation of gases, leading to their conversion to stable and selective chemical reagents, will open novel opportunities for preparative synthesis. With the visible progress in molecular containers for gases, novel catalytic systems for gas conversion are on the way. Supramolecular materials that involve multiple, preorganized cavities, capsules and nanotubes will introduce better selectivities in gas separation and stabilities in gas storage. Polymers from gases are also promising. Gases can now be used as building blocks. Considering the significance of gases in the environment, these strategies offer means for creating environmentally responsive processes and technologies. Reversible, dynamic polymers from gases, with switchable properties, should be of interest as separating materials and also for storage and release of biologically active compounds. All these and other developments, with no doubts, will be seen in the nearest future.

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