This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Molecular Containers for NO<i>X</i> Gases

Dmitry M. Rudkevich[a]; Yanlong Kang[a]; Alexander V. Leontiev[a]; Voltaire G. Organo[a]; Grigory V. Zyryanov[a]

[a] Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX, USA

To cite this Article Rudkevich, Dmitry M. , Kang, Yanlong , Leontiev, Alexander V. , Organo, Voltaire G. and Zyryanov, Grigory V.(2005) 'Molecular Containers for NO<i>X</i> Gases', Supramolecular Chemistry, 17: 1, 93 — 99

To link to this Article: DOI: 10.1080/10610270412331328808

URL: http://dx.doi.org/10.1080/10610270412331328808

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Supramolecular Chemistry, January–March 2005 Vol. 17 (1–2), pp. 93–99

Taylor & Francis
Taylor & Francis Group

Molecular Containers for NO_X Gases

DMITRY M. RUDKEVICH*, YANLONG KANG, ALEXANDER V. LEONTIEV,
VOLTAIRE G. ORGANO and GRIGORY V. ZYRYANOV

Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX 76019-0065, USA

Received (in Austin, USA) 23 July 2004; In final form 2 September 2004

Supramolecular approaches to visual detection, storage, conversion and use of NO_X gases are described that deploy calixarenes and their derivatives, such as hemicarcerands and synthetic nanotubes. Polymer-supported calixarene materials for NO_X are also introduced. Chemical fixation of NO_2/N_2O_4 is demonstrated through the transformation into calixarene–NO^+ complexes and their use as nitrosonium storing and releasing reagents for organic synthesis. These findings highlight perspectives of supramolecular chemistry and molecular recognition in sensing and fixation of environmentally important gases.

Keywords: Calixarenes; Nitrogen oxides; Polymers; Sensors; Supramolecular chemistry

INTRODUCTION

Molecular containers are synthetic receptor molecules that possess inner cavities [1–4]. They mimic hydrophobic pockets of enzymes and can entrap smaller guest-species, stabilize reactive intermediates, catalyze some reactions and potentially transport/deliver drug molecules. We use molecular containers for sensing, fixation and storage of gases. Supramolecular chemistry of gases is in its early stage, but has made significant progress [5,6]. Technically, gases are more difficult to handle than liquids and solids. Their molecules are neutral and relatively apolar. Electrostatic binding interactions with gases are much less effective than with ions and polar organic guests. Furthermore, gases are small, of a 2–4 Å^3 range. Accordingly, a higher degree of design is required to achieve complementarity. Often, a combination of different binding forces is necessary.

We are particularly interested in NO_X gases—the sum of nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), N_2O_3, dinitrogen tetroxide (N_2O_4) and N_2O_5 [7]. N_2O is a major greenhouse gas, and also a blood gas; it is heavily used in anesthesia. NO serves as an important messenger in signal transduction processes. Higher nitrogen oxides are extremely toxic pollutants and participate in the formation of ground-level ozone and global warming. NO_X are aggressively involved in various nitrosation processes in biological tissues and cause mutations. According to the United States Environmental Protection Agency, national emissions of NO_X have increased over the past 20 years by 4% [7]. Extensive NO_X circulation requires their systematic monitoring under a variety of conditions and also necessitates the development of improved methods of their fixation, chemical conversion and utilization. In this review, we describe a supramolecular approach to the problem, which involves reversible intermolecular interactions and assemblies. We overview basic principles towards encapsulation and conversion of NO_X gases within molecular containers and describe our experimental advances in this direction. Potential applications of encapsulated gas complexes are also discussed for the design of novel reaction chambers for gas fixation, as well as supramolecular gas sensors and gas storing, releasing and separating materials.

ENCAPSULATION OF N_2O

N_2O is widely considered a noncoordinating gas, and its complexes, even with organometallic compounds, are extremely rare. Encapsulation of N_2O in

---

*Corresponding author. E-mail: dmrudkev@exchange.uta.edu

ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/10610270412331328808

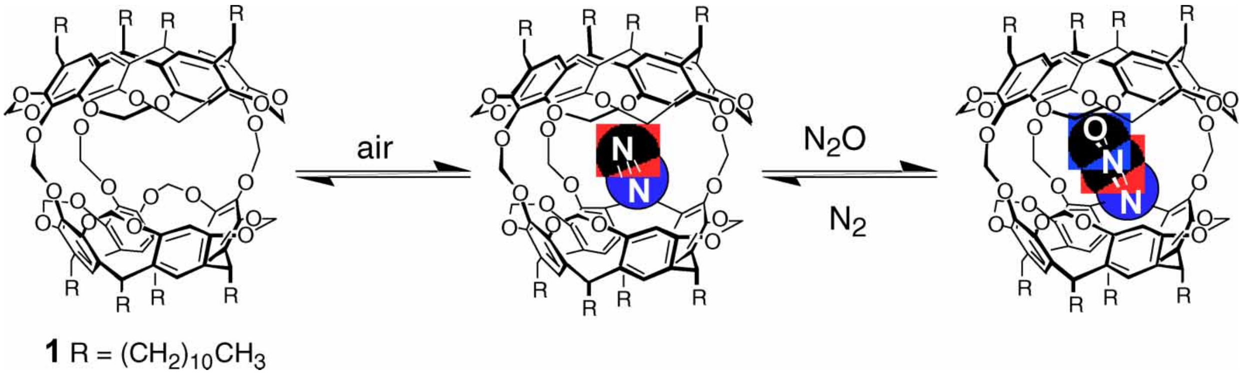


FIGURE 1 Encapsulation of N_2O in hemicarcerand **1** in solution and in the solid state [10].

molecular containers may be very useful in the fabrication of gas storing/releasing materials for anesthesia. Early encapsulation complexes with N_2O include clathrate hydrates [8] and porous coordination polymers [9]. We have used well-defined molecular containers [10].

Hemicarcerand **1** (Fig. 1) was first prepared by Cram and coworkers more than a decade ago [1]. It possesses two resorcin[4]arene hemispheres, connected by three methylene bridges. The inner cavity volume is $\sim 110\,\text{Å}^3$. The remaining gap between the two hemispheres allows for reversible encapsulation of benzene-size guest molecules; the solvent in this case is too bulky to enter the cavity.

We found that empty hemicarcerand **1** instantly absorbed N_2 from the atmosphere, even in the solid state. Bubbling N_2O through chloroform or benzene solutions of **1** resulted in the quantitative formation of **1**·N_2O complex. With the N_2O volume of $47\,\text{Å}^3$, the packing coefficient of 38% was estimated and a 1:1 stoichiometry was suggested.

The exchange of N_2O in and out of the cavity is slow on the NMR time-scale, with both free and filled host signals seen separately (at room temperature). This implies that the N_2O decomplexation energy barrier is at least $15\,\text{kcal mol}^{-1}$. N_2O, CO_2, N_2, H_2 and He replace each other in the inner cavity of **1**, which cannot be easily achieved in conventional encapsulation studies with liquid and solid guests.

Solid **1**·N_2O complex was readily obtained by simply bubbling the gas through solutions of **1** in chloroform or benzene until complete dryness. The solid is indefinitely stable under the N_2O atmosphere, but loses the gas upon exposure to air. The half-life of solid hemicarceplexes **1**·N_2O is ~ 30 min. Gases replace each other in the solid state as well. For example, upon flashing a powder containing **1** and **1**·N_2 with dry N_2O, powdered **1**·N_2O was obtained quantitatively.

In summary, elusive N_2O can be trapped in a molecular container. Using organic synthesis, the dimensions and portals of the container can be further modified to achieve greater selectivity in separation and stability in storage. Polymeric N_2O-storing and releasing materials can also be prepared. There is also the hope that cavity-containing solids can be used to store and release other important gases.

NO_X AND CALIX[4]ARENES

The major drawback of reversible encapsulation complexes with gases lies in their low thermodynamic stability. Even well-preorganized cavities cannot complex strongly, due to the lack of binding interactions. An alternative approach is based on reversible chemical transformation of gases upon complexation. In this case, they produce reactive intermediates with higher affinities to the receptor molecules.

Rathore *et al.* showed that when converted to the cation-radical, calix[4]arene **2** was able to strongly complex NO gas with the formation of cationic calix-nitrosonium species **3** [11]. In these, the NO molecule is transformed into the nitrosonium cation (NO^+) (Fig. 2). Strong charge-transfer interactions between NO^+ and the π-surface of **2** placed the guest molecule between the cofacial aromatic rings at a distance of 2.4 Å, much shorter than the typical van der Waals contact (3.2 Å). The association constant $K_{\text{assoc}} > 5 \times 10^8\,\text{M}^{-1}$ was determined (in CH_2Cl_2). On the other hand, NO^+ was easily released from the cavity upon addition of Cl^- anions, due to the formation of nitrosyl chloride (NOCl). As charge-transfer complex **3** is deeply colored, this can be used for colorimetric NO sensing.

We have studied host–guest complexes formed upon reversible interaction between NO_2 and simple calix[4]arenes [12,13]. NO_2 is a paramagnetic gas of an intense brown-orange color. It exists in equilibrium with the colorless N_2O_4. The dynamic interconversion between NO_2 and N_2O_4 makes it impossible to study either of these species alone. On the other hand, N_2O_4 may disproportionate to

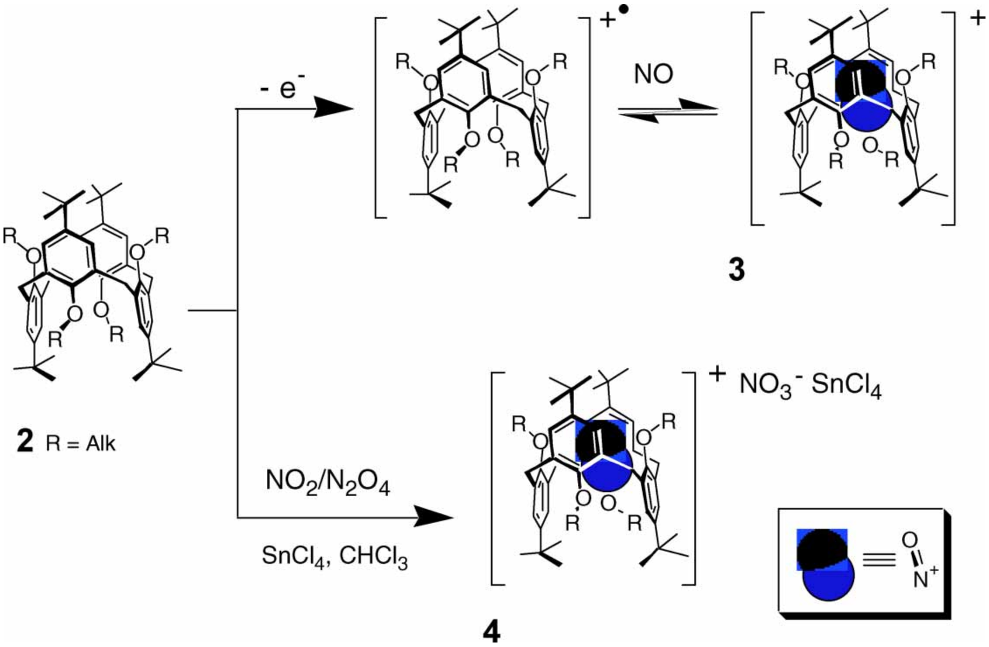


FIGURE 2 Chemical reactions between NO, NO_2/N_2O_4 and calix[4]arene **2**. Formation of encapsulated nitrosonium complexes **3** [11] and **4** [12,13]. Other calix[4]arene conformers showed similar behavior; the corresponding complexes were also isolated and characterized.

ionic $NO^+NO_3^-$ while interacting with simple aromatic derivatives [14]. We showed that calixarenes react with NO_2/N_2O_4 to form stable nitrosonium complexes, for example **4** (Fig. 2). These complexes are deeply colored and can dissociate upon addition of water or alcohols. NO_2/N_2O_4 are very aggressive and may further nitrosate/nitrate calixarenes. More stable calixarene-nitrosonium complexes were isolated upon addition of Lewis acids such as $SnCl_4$ and $BF_3{-}Et_2O$. Independent structural evidence for **3** and **4** came from the complexation experiments between calixarene **2** and commercially available $NO^+SbCl_6^-$ and $NO^+SbF_6^-$ salts. The corresponding UV–vis, FTIR and ^1H NMR complexation-induced changes were analogous to those previously obtained with NO and NO_2 gases [11–13].

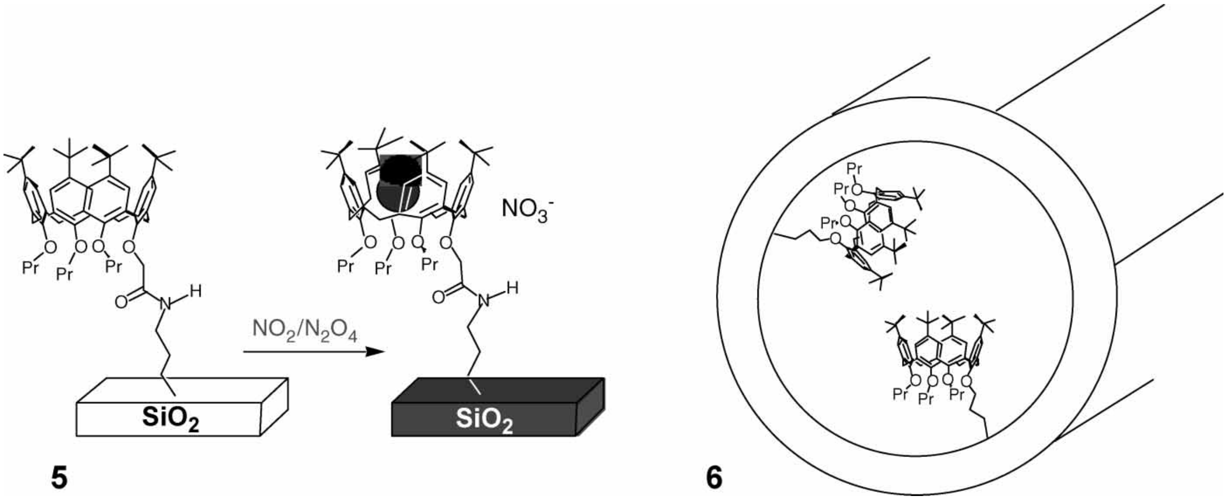
The visible spectrum of complex **4** showed a broad charge-transfer band at λ_{max} ~560 nm ($\varepsilon = 8 \times 10^3\,M^{-1}\,cm^{-1}$). While neither calixarenes nor NO_2 absorb in this region, addition of as little as ~1 eq NO_2 to the solution of **2** in chlorinated solvent results in the appearance of the charge-transfer band [15]. Its absorbance increases upon addition of larger quantities of NO_2 and reaches saturation when ~10 eq NO_2 is added. Accordingly, calixarenes can detect NO_2 at µm/ppm concentrations.

MATERIALS FOR NO_X SENSING AND FIXATION

Current NO_2 sensors are mostly electrochemical and monitor changes in potential upon exposure of metal surfaces to NO_2 (see for example [15]). In many cases, however, other gases, such as moisture, O_2, HCl, HBr, SO_X and NH_3, significantly influence the detection selectivity and therefore sensitivity. Optical sensors, which are based on the coloration chemical reaction between NO_2 and certain organic compounds, are more selective. At the same time, reversibility is not easy to achieve. As mentioned, interactions between calix[4]arenes and NO_2 possess a number of unique features. They are very stable but reversible, result in dramatic color changes, and are unique and specific for NO_2. This can be used for the gas detection in the presence of other gases/vapors. Even NO gas does not react with calixarenes prior their oxidation [11].

Apart from sensing, calixarenes may be used as traps for NO_2 and other NO^+ ions generating NO_X, especially NO/O_2, NO/air and N_2O_3. Such procedures are required in the purification of commercial gases, especially NO for medical purposes.

Accordingly, calixarene-based materials have been prepared for sensing and entrapment of NO_X. In the first generation, silica was successfully used as a platform for the calixarene immobilization (Fig. 3). Calix-silica gel **5** was obtained from commercial 3-aminopropylated silica gel (Aldrich) and the appropriately functionalized calix[4]arene module [13]. Loading of ~17% was achieved. Expanding our approach, Liu *et al.* recently prepared calix[4]arene-based periodic mesoporous silica **6** [16]. According to the adsorption/desorption and TEM studies, the maximum pore dimension in **6** is 2.9 nm.



5 **6**

FIGURE 3 Calixarene-based silica materials for sensing and entrapment of NO_X [13,16].

In the NO_2 entrapment experiments, a stream of the gas was passed through pipettes loaded with materials **5** and **6**, instantly producing a dark purple color, indicating NO^+ complexation [13,16]. This was confirmed by FTIR spectroscopy, where the characteristic calixarene–NO^+ stretch was observed at $\nu \sim 1920\,cm^{-1}$. The solid-supported complexes were stable for hours, especially for the mesoporous silica material **6**. In this case, the NO^+ complexation was also detected by CHN analysis. The materials can be regenerated by simply washing with alcohol and can then be used again.

NITROSATING REAGENTS

Calixarene-nitrosonium complex **4** and its analogs can release NO^+ and thus act as nitrosating agents [17]. In synthetic organic chemistry, nitrosation is of particular importance. Alkyl nitrites, nitrosamines/amides and nitrosothiols are used in biomedicine as NO-releasing drugs. In total synthesis and methodology, $-N{=}O$ is an important activating group, allowing elegant transformations of amides to carboxylic acids and their derivatives. In addition, nitrosation mimics interactions between biological tissues and NO_X gases. We discovered that secondary amides **7** reacted with complex **4** and its relatives with remarkable selectivity [17]. The chemical properties of the encapsulated NO^+ are different from those in bulk solution and are controlled by the cavity. These are encapsulated reagents.

The cavity in complex **4** protects highly reactive NO^+ species from the bulk environment. Indeed, this complex is quite stable towards moisture and oxygen, and can be handled for at least several days without dry box conditions and/or a N_2 atmosphere. On the other hand, it can be decomposed within a few minutes by the addition of larger quantities of H_2O or alcohols, recovering the free calixarene.

When mixed with an equimolar solution of amide $R'C(O)NHR$ **7** in $CHCl_3$, complex **4** reacted quickly at room temperature, yielding up to 95% of *N*-nitrosamides **8** (Fig. 4). Dark blue solutions of **4** discharged upon addition of amide substrates, which is a reasonable visual test for the reaction. Among the variety of amides **7**, only those possessing *N*$-CH_3$ substituents were transformed to the corresponding *N*-nitrosamides **8**. No reaction occurred for substrates possessing bulkier groups. As a consequence, no color discharge was observed.

Tight but reversible encapsulation of NO^+ species thus offers size-shape selectivities, previously unknown for existing, more aggressive nitrosating agents. NO^+ species, generated from NO^+-salts, N_2O_3, NO_2/N_2O_4, NO/O_2, NO/air, $NaNO_2/H_2SO_4$ etc., are typically not selective.

Polymer-supported nitrosating reagents have also been prepared [15]. Among the advantages of such reagents are the ease of their separation from the reaction mixture, their recycling, and the simplification of handling toxic and odorous NO_X gases. Particularly useful are soluble polymers, as they overcome problems associated with the heterogeneous nature of the reaction conditions.

The PEG-supported polymer **9** was synthesized; it is robust and soluble in organic solvents [15]. Deep purple NO^+-storing material **10** was then obtained by simply bubbling NO_2/N_2O_4 through a solution of **9** in CH_2Cl_2 for 2–3 min, followed by brief flashing with N_2 to remove the remaining NO_2/N_2O_4 gases. Material **10** effectively nitrosated amides **7** in CH_2Cl_2; preference for the less bulky N–Me amide was again observed. We are currently preparing

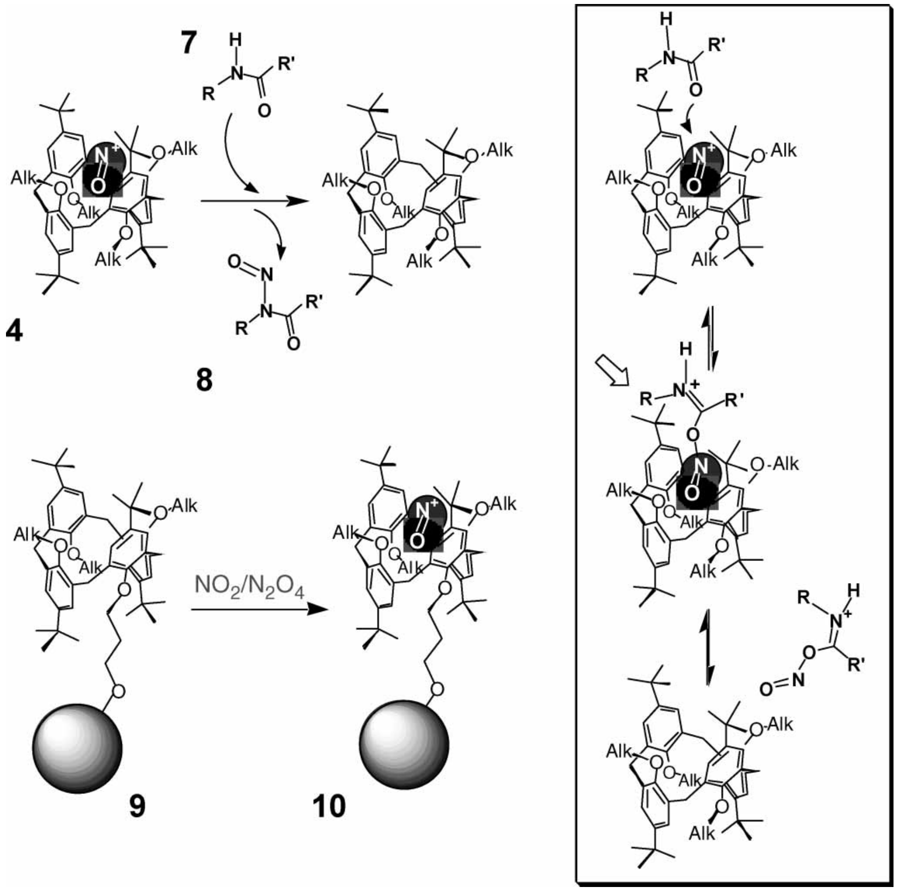


FIGURE 4 Encapsulated calixarene-based reagents and nitrosation of secondary amides [15,17]. The currently accepted mechanism incorporates an initial electrophilic attack of NO^+ on the nucleophilic carbonyl oxygen of **7**, yielding the corresponding *O*-nitroso species (on the right) [18,19]. This places the *N*–R group in close proximity to the bulky calixarene rim. For a sizeable R-group, this situation is sterically unfavorable. Because of the extremely strong binding of NO^+ by the calixarene, the rate-limiting formation of the *O*-nitrosation intermediates should take place within the cavity, prior to the NO^+ dissociation.

more robust, silica-based encapsulated reagents for nitrosation.

TOWARDS SYNTHETIC NANOTUBES

Recent studies have shown that gases can be stored inside single-walled carbon nanotubes (SWNTs) [6]. Entrapping isotopes of Noble gases by SWNTs may improve their use in medical imaging. SWNTs encapsulate N_2, O_2, NO and CF_4. Storage of H_2 in SWNTs is extremely promising in the design of energy-rich fuel-cell electric devices and is currently under intense investigation. Synthetic nanotubes are very rare, and their supramolecular chemistry with gases is not yet known. Organic synthesis permits much greater structural variations and control over the tube length/diameter, which is important for the gas dynamics and the design of potential gas storing chambers and conversion/catalytic vessels. We recently designed synthetic tubes for NO_2/N_2O_4 fixation, which are based on calixarenes.

In the nanotube design, 1,3-alternate calix[4]arenes are rigidly connected from both sides of their rims with pairs of diethylene glycol linkers (Fig. 5). In this calixarene conformation, two pairs of phenolic oxygens are oriented in opposite directions, providing a diverse route to modularly enhance the tube length. The bridge length is optimal: it not only provides relatively high conformational rigidity of the tubular structure but also seals the walls, minimizing the gaps between the calixarene modules. The calixarene tubes possess defined inner tunnels of $\sim 5\,\text{Å}$ diameter and may entrap multiple NO^+ molecules, one in each cavity.

Shorter nanotubes, containing two and three calixarene modules, have been previously synthesized and tested for gas entrapment. For example, exposure of tube **11** to NO_2/N_2O_4 in chlorinated solvents results in the rapid encapsulation of NO^+ cations within its interior (Fig. 6) [20]. The corresponding mono- and dinitrosonium complexes were isolated and characterized by UV–vis, FTIR and ^{1}H NMR spectroscopies, and also by molecular modeling. The NO^+ entrapment process is reversible, and addition of water quickly recovered starting tube **11**. As in the simpler

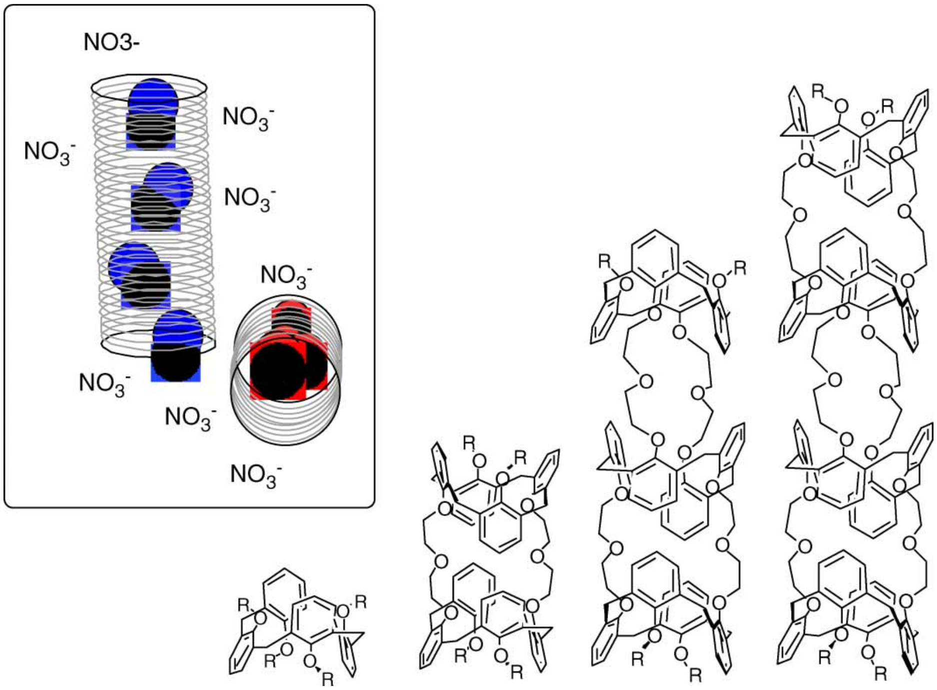


FIGURE 5 Molecular nanotubes for NO_2/N_2O_4 fixation. Upon exposure to polyaromatic surfaces of the tubes, N_2O_4 disproportionates to $NO^+NO_3^-$. Nanotubes encapsulate NO^+ within their interiors. In-and-out exchange of trapped NO^+ species is possible, and this can be applied for nitrosation reactions.

complex **4**, NO^+ species encapsulated within the tube act as nitrosating agents for secondary amides.

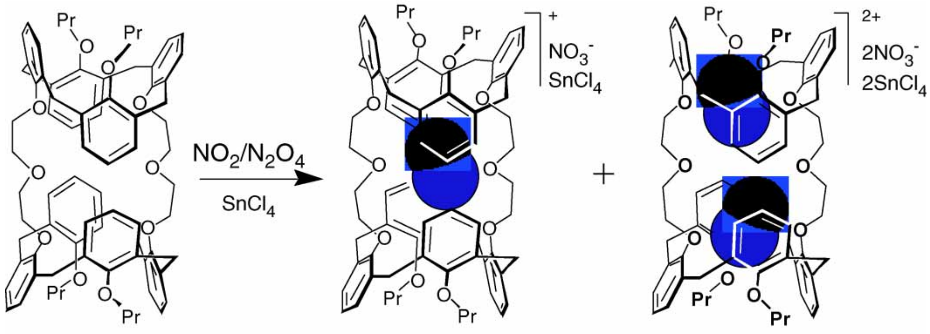
Synthesis of longer, polycalixarene-containing nanotubes is under way. In contrast to cavitands, carcerands and capsules [1–4], the supramolecular chemistry of synthetic nanotubes is unexplored. It would be interesting to see how multiple guests move and communicate with each other inside the nanotubes.

CONCLUSIONS

Supramolecular chemistry of environmentally and industrially important gases is developing rapidly, and novel sensing and fixation processes for NO_X are currently available. These use calixarenes and are based on solid materials. Synthetic nanotubes for NO_2/N_2O_4 have also been introduced. Nitrosonium complexes of calixarenes can be used as vehicles for nitrosonium transfer and encapsulated nitrosating reagents for synthetic methodology. We are currently applying similar supramolecular strategies towards other important gases [21,22].

Acknowledgements

The research described here was supported by the National Science Foundation (CHE-0350958), the Texas Advanced Technology Program (003656-0146-2003), the Petroleum Research Fund (37440-AC4), administered by the American Chemical Society,



11

FIGURE 6 Calix[4]arene-based tube **11** reacts with NO_2/N_2O_4 with the formation of nitrosonium complexes [20]. Multiple-guest complexes are expected with tube elongation.

the American Cancer Society Institutional Research Grant to the University of North Texas Health Science Center (IRG-01-187-01-021), the Alfred P. Sloan Foundation, and the University of Texas at Arlington.

References

[1] Cram, D. J.; Cram, J. M. *Container Molecules and their Guests*; Royal Society of Chemistry: Cambridge, 1994.

[2] Rudkevich, D. M. *Bull. Chem. Soc. Jpn* **2002**, *75*, 393.

[3] Jasat, A.; Sherman, J. C. *Chem. Rev.* **1999**, *99*, 931.

[4] Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, Jr., J. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1488.

[5] Rudkevich, D. M. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 558.

[6] Rudkevich, D. M.; Leontiev, A. V. *Aust. J. Chem.* **2004**, *57*, 713.

[7] US EPA publications. Available online at: www.epa.gov/air/urbanair/nox/index.html.

[8] Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press, Oxford, New York, 1997.

[9] Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 2334.

[10] Leontiev, A. V.; Rudkevich, D. M. *Chem. Commun.* **2004**, 1468.

[11] Rathore, R.; Lindeman, S. V.; Rao, K. S. S.; Sun, D.; Kochi, J. K. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 2123.

[12] Zyryanov, G. V.; Kang, Y.; Stampp, S. P.; Rudkevich, D. M. *Chem. Commun.* **2002**, 2792.

[13] Zyryanov, G. V.; Kang, Y.; Rudkevich, D. M. *J. Am. Chem. Soc.* **2003**, *125*, 2997.

[14] Bosch, E.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 3314.

[15] Kang, Y.; Rudkevich, D. M. *Tetrahedron*, **2004**, *60*, 11219.

[16] Liu, C.; Fu, L.; Economy, J. *Macromol. Rapid Commun.* **2004**, *25*, 804.

[17] Zyryanov, G. V.; Rudkevich, D. M. *Org. Lett.* **2003**, *5*, 1253.

[18] Darbeau, R. W.; Pease, R. S.; Perez, E. V. *J. Org. Chem.* **2002**, *67*, 2942.

[19] Birney, D. M. *Org. Lett.* **2004**, *6*, 851.

[20] Zyryanov, G. V.; Rudkevich, D. M. *J. Am. Chem. Soc.* **2004**, *126*, 4264.

[21] Xu, H.; Rudkevich, D. M. *Chem. Commun.* **2003**, 2828.

[22] Hampe, E. M.; Rudkevich, D. M. *Tetrahedron* **2003**, *59*, 9619.