

Sensing and Fixation of NO₂ by CalixarenesKUI 4/2005
Received March 9, 2004
Accepted May 17, 2004

D. M. Rudkevich*

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

In this short review, an approach towards visual detection, conversion and use of NO₂ is described, which applies methods and techniques of supramolecular chemistry and employs calix[4]arenes. Exposure of alkylated calix[4]arenes to NO₂ / N₂O₄, both in chlorinated solvents and in the solid state, results in deeply colored calixarene-nitrosonium (NO⁺) complexes. NO⁺ were found encapsulated within the calixarene cavities, and stable charge-transfer complexes resulted with $K_{\text{assoc}} > 10^6 \text{ dm}^3 \text{ mol}^{-1}$ (CDCl₃). The complexation process is reversible, and the complexes dissociate upon addition of water and alcohol, recovering the parent calixarenes. Attachment of calix[4]arenes to silica gel was demonstrated, which afforded a solid material for visual detection and entrapment of NO₂ / N₂O₄. Design and synthesis of calixarene-based nanotubes for trapping NO₂ / N₂O₄ was proposed. Chemical utilization of NO₂ / N₂O₄ was demonstrated through the transformation into calixarene-NO⁺ complexes and their use as nitrosonium storing and transferring reagents for organic synthesis. These findings open wider perspectives towards NO₂ / NO_x sensing, storing and converting materials.

Keywords: Calixarenes, nitrogen oxides, polymers, sensors, supramolecular chemistry

Introduction

Nitrogen dioxide (NO₂) is a major component of so-called NO_x gases.^{1,2} NO_x is the sum of nitric oxide (NO), NO₂, N₂O₃, N₂O₄ and other oxides of nitrogen. These are toxic atmospheric pollutants derived from fossil fuel combustion, power plants, and large-scale industrial processes. NO_x are involved in the formation of ground-level ozone, participate in global warming, and also form toxic chemicals and acid rain/aerosols. NO_x are aggressively involved in various nitrosation processes in biological tissues.³ Being free radical, NO rapidly reacts with oxygen, producing N₂O₃ (e.g., NO · NO₂) and NO₂/N₂O₄. These are powerful nitrosating agents, both, in the gas phase and in solution. The pathophysiological significance of NO_x derives from their ability to generate mutagenic nitrosopeptides and further diazo-peptides, to produce carcinogenic nitrosoamines, and to nitrosate and further deaminate DNA nucleobases. According to The United States Environmental Protection Agency,¹ national emissions of NO_x have increased over the past 20 years by 4 %. Tolerable levels of NO_x are $w \leq 5 \cdot 10^{-6}$ ppm.

Extensive NO₂ circulation in the atmosphere requires its systematic monitoring under variety of conditions and also necessitates the development of improved methods for its fixation, chemical conversion and utilization. In this review article, we describe a *supramolecular approach* to the problem. We present host-guest complexes, formed upon reversible interaction between NO₂ and simple calix[4]arenes (Fig. 1). We show that calixarenes react with NO₂ to form stable nitrosonium (NO⁺) complexes. These calixarene-

NO⁺ complexes are deeply colored and can dissociate upon addition of water. These complexes can be utilized for the NO⁺ transfer processes and nitrosation reactions. Accordingly, our findings offer novel processes of NO₂ visual sensing and chemical utilization. They may also lead towards supramolecular NO₂-storing materials.

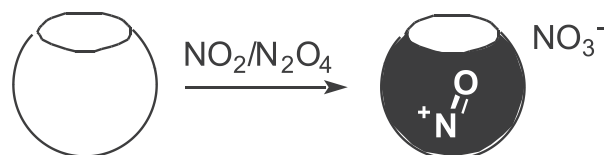


Fig. 1 – Chemical sensing and fixation of NO₂/N₂O₄ with calix[4]arenes, a cartoon representation

Calix[4]arenes and their complexes

Calix[4]arenes are popular building blocks in molecular recognition. They are widely used in the construction of molecular receptors, sensors and container-molecules.⁴ Cone-shaped calix[4]arenes are $\sim 4 \text{ \AA}$ ($\sim 0.4 \text{ nm}$) deep and $\sim 7 \text{ \AA}$ ($\sim 0.7 \text{ nm}$) in diameter at the upper rim (see **1**, Fig. 2). Calix[4]arenes in a 1,3-alternate conformation possess a cylindrical inner tunnel, defined by two cofacial pairs of aromatic rings oriented orthogonal along the cavity axis (see **2**, Fig. 2). According to the X-ray studies, this tunnel is $\sim 5\text{--}6 \text{ \AA}$ ($\sim 0.5\text{--}0.6 \text{ nm}$) in diameter.

NO₂ is a paramagnetic gas of an intense brown-orange color. It forms easily the colorless dimer, dinitrogen tetroxide (N₂O₄). Bonding in N₂O₄ is quite weak, and as the temperature raises, it rapidly dissociates back to NO₂. The position of the equilibrium between the two compounds varies with temperature. The dynamic interconversion between

* Corresponding author. Tel: + 817 272 5245; fax: + 817 272 3808; e-mail: rudkevich@uta.edu

NO₂ and N₂O₄ makes it impossible to study either of these species alone. On the other hand, N₂O₄ may disproportionate to ionic NO⁺NO₃⁻ while interacting with aromatic compounds.⁵

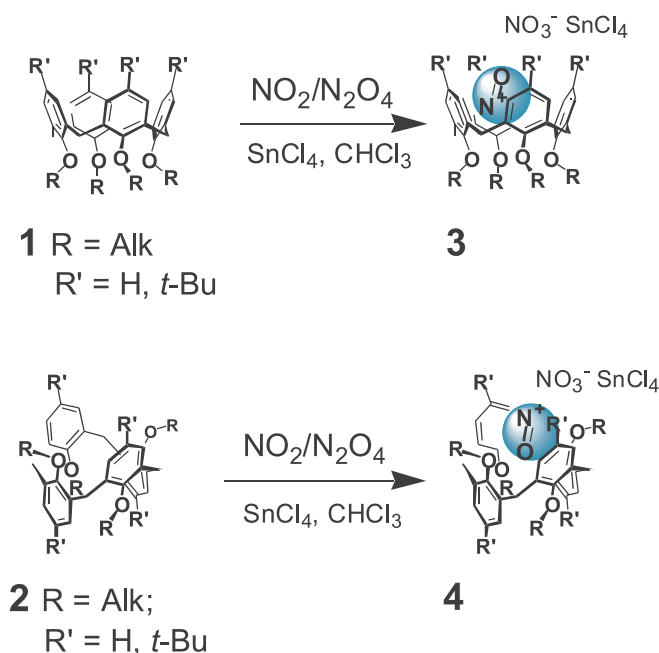


Fig. 2 – Chemical reaction between NO₂/N₂O₄ and calix[4]arenes **1** and **2**. Formation of encapsulated nitrosonium complexes **3** and **4**

We found that calix[4]arenes **1** and **2** reversibly interact with NO₂/N₂O₄ with the formation of deeply colored species (Fig. 2, Fig. 3).^{6,7} Specifically, **1** and **2** facilitate disproportionation of N₂O₄, and then entrap highly reactive NO⁺ cations within their cavities. Very stable nitrosonium complexes **3** and **4** were formed, which were *quantitatively* isolated upon addition of a Lewis acid SnCl₄ (Fig. 2). It is known that Lewis acids stabilize arene-nitrosonium charge-transfer complexes.¹⁵ Only one NO⁺ cation was found per cavity. Very high $K_{\text{assoc}} \gg 10^6 \text{ dm}^3 \text{ mol}^{-1}$ were determined (chlorinated solvent, UV-Vis, NMR). Complexes **3** and **4** were characterized by various spectroscopic techniques and CHN elemental analysis.

The UV-Vis spectra showed broad charge-transfer bands at $\lambda_{\text{max}} \sim 550 \text{ nm}$, and the FTIR spectra exhibited characteristic arene-NO⁺, stretching at $\nu \sim 1950 \text{ cm}^{-1}$. The ¹H NMR spectra of **3** and **4** showed new sets of the calixarene signals.

For example, the ¹H NMR spectrum of **4** (R = (CH₂)₅CH₃, R' = *t*-Bu) showed new sets of the calixarene signals, different from **2** (R = (CH₂)₅CH₃, R' = *t*-Bu) (Fig.

4).⁸ In particular, aromatic CH protons of guest-free **2** were seen as a singlet at 6.95 ppm. In nitrosonium complex **4**, it was *trans-*formed into a singlet at 7.02 ppm. The methylene bridge CH₂ protons of **2** were recorded as a singlet at 3.73 ppm. In complex **4**, this was seen at 3.60 ppm.

Complexes **3**, **4** can be obtained from calixarenes **1**, **2** and NO₂/N₂O₄ even without SnCl₄ (see for example, Fig. 4C), however their stability is lower.

Independent structural evidence for **3**, **4** came from the complexation experiments between calixarenes **1**, **2** and

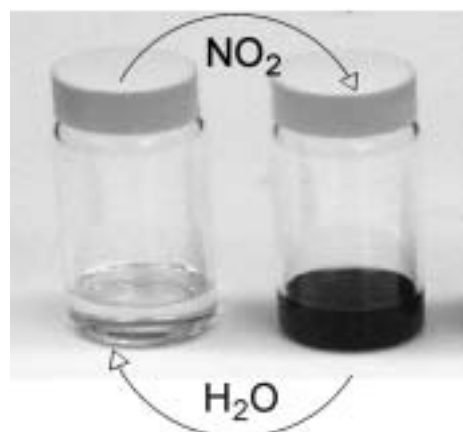


Fig. 3 – Color changes upon interaction of NO₂/N₂O₄ with calix[4]arenes (in chlorinated solvents)

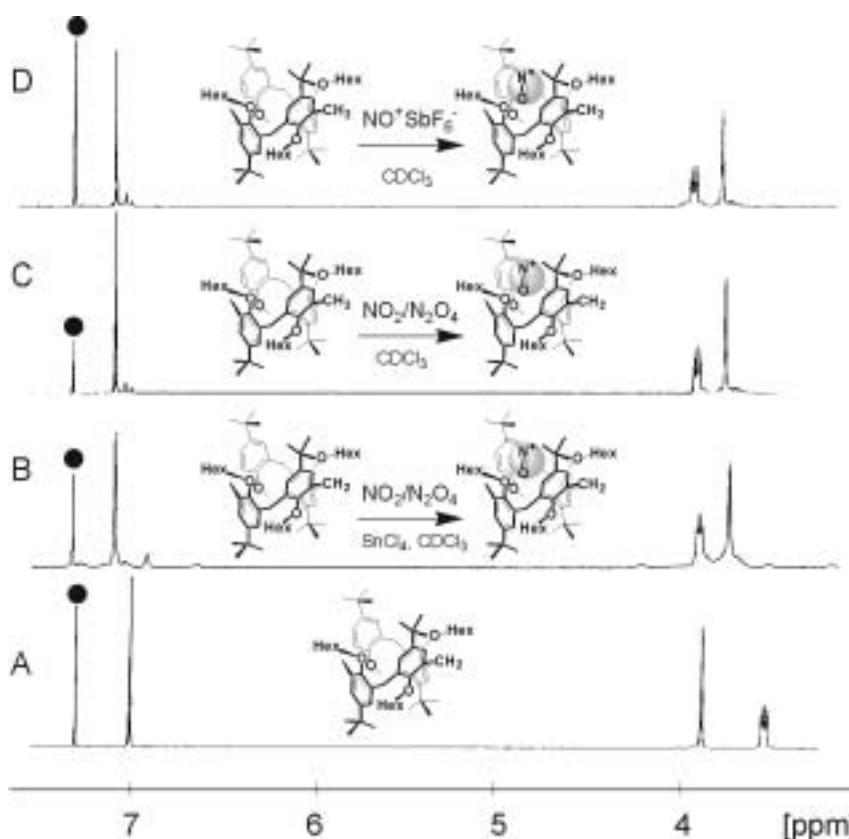


Fig. 4 – Portions of the ¹H NMR spectra (500 MHz, CDCl₃, 295 ± 1 K) of a calix[4]arene and its nitrosonium complexes, prepared by three different methods. The residual CHCl₃ signals are marked "•".

commercially available NO⁺SbF₆⁻ salt (CDCl₃, 295 K). The corresponding UV-Vis, FTIR and ¹H NMR complexation induced changes were in agreement with the data presented above for complexes **3** and **4** (see for example, Fig. 4D).⁹

In the control experiments with non-cyclic anisole (e.g., methoxybenzene), only weak coloration was observed upon exposure to NO₂. Moreover, when structurally similar calixarenes, with *blocked* cavities, were tested, no coloration was observed either; there was no indication for complexation in the UV-Vis and ¹H NMR spectra. These experiments emphasize the importance of the calixarene cavities in the described transformations and rule out the possibility of the NO⁺ coordination outside the cavity.

At the same time, the complexation process is reversible, and the NO⁺ guest can still leave the calixarene cavity. Addition of H₂O to the freshly prepared CHCl₃ solutions of **3**, **4** resulted in the complete dissociation and recovery of calixarenes **1**, **2**. The color quickly disappeared (Fig. 3).

Toward materials for NO₂ sensing and fixation

Thus found interactions between calix[4]arenes and NO₂ possess a number of unique features. They a) are reversible, b) result in dramatic color changes, and c) are unique and *specific* for NO₂. The latter could be rather useful for the gas detection in the presence of other gases such as H₂O, O₂, HCl, HBr, SO_x, and NH₃. None of those reacts with calixarenes. Neat nitric oxide (NO) also does not react. In their work on the NO sensing by tetra-*O*-alkylated calix[4]arenes,⁹ Kochi and Rathore showed, that calixarenes had to be oxidatively activated and form the corresponding cation-radicals, prior complexing NO.

Current NO₂ sensors are mostly electrochemical and monitor changes of potential upon exposure metal surfaces to NO₂.¹⁰ In many cases however, other vapors – H₂O, O₂, HCl, HBr, SO_x, and NH₃ significantly influence the detection selectivity and therefore sensitivity. Optical sensors, which are based on coloration reaction between NO₂ and certain organic compounds, are more selective as the reactions are specific.¹¹ At the same time, reversibility of such sensing processes is not easy to achieve.

For potential application in sensing technology, receptor molecules must not only be synthetically available, but also readily immobilizable on larger (macro)molecules, solid supports or surfaces. A wide variety of polymers and nanomaterials are now commercially available. We used 3-aminopropylated silica gel from Aldrich and functionalized it with calixarene modules.⁷ Calixarene silica gel **5** was thus obtained. As follows from molecular modeling, calix[4]arene fragments are ~ 1 × 1 nm (~ 10 × 10 Å) in their dimensions, so their attachment *via lower rim* should guarantee the proper configuration of the *upper rim* to sufficiently respond to the presence of the gas analyte.

In the NO₂ entrapment experiments, stream of the gas was passed through Pasteur pipettes, loaded with the calixarene-based silica gel **5** (Fig. 5). In one pipette, dry silica gel **5** was loaded, and the other contained **5** pre-wetted with CHCl₃. Both silica gels instantly turned dark purple, indicating the NO⁺ complexation. The color of the wetted material appeared to be deeper and it stayed for hours. The dry material bleached within minutes. The FTIR spectrum, recorded in KBr discs, gave weak but reproducible stretch at $\nu \sim 1920 \text{ cm}^{-1}$, indicating the presence arene-NO⁺ complexes. No coloration was observed for the pipette loaded with the starting, 3-aminopropylated silica gel. This once

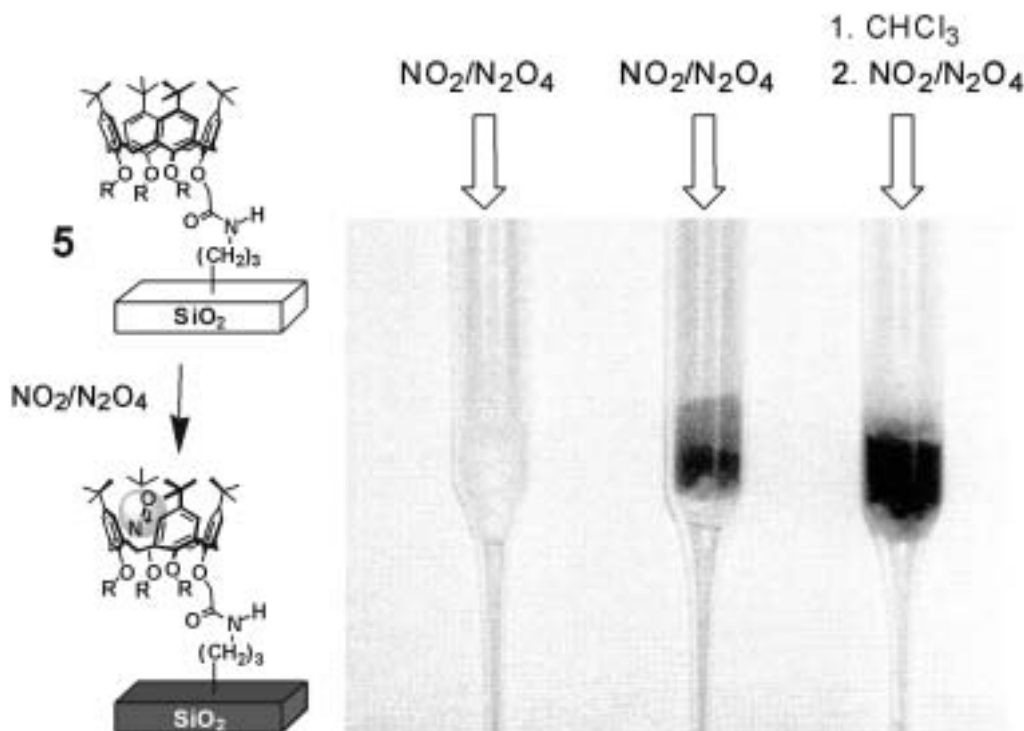


Fig. 5 – Calix[4]arene functionalized silica gel **5** traps NO₂. The columns were prepared as follows: a) loaded with starting aminopropyl functionalized silica gel; b) loaded with the calixarene-based dry silica gel **5**; c) loaded with silica gel **5** and flashed with CHCl₃. All three columns were then flashed with NO₂ (~30 s), and the pictures were made after ~2–3 min afterwards.

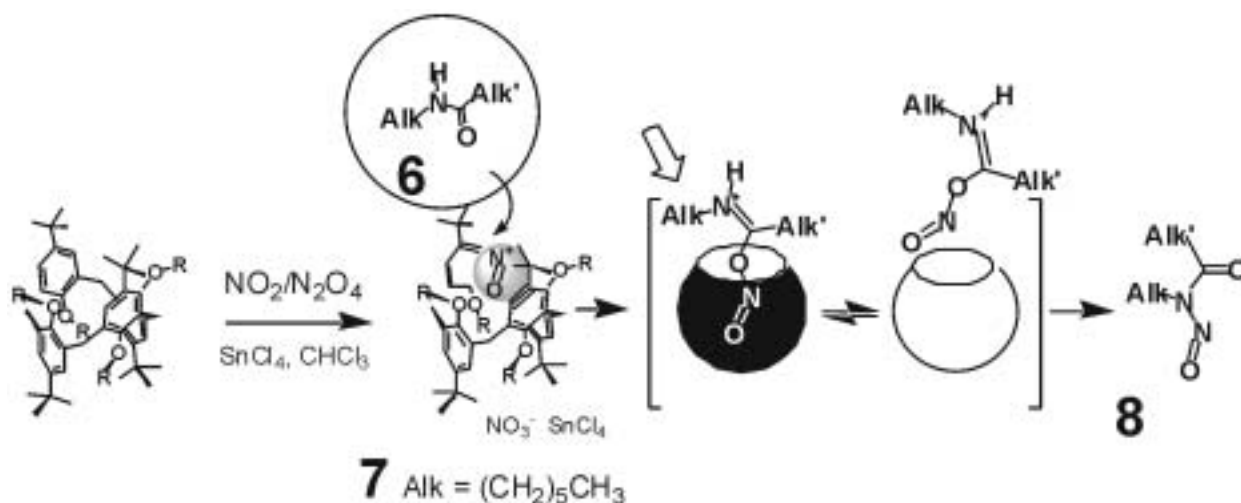


Fig. 6 – Encapsulated nitrosating reagent **6** and its reaction with amides.

again emphasizes the role of calixarene cavities in the described processes.

Although requiring further synthetic optimization, silica gel **5** may still be used for NO₂ detection and even for purification of other nitrogen oxides, especially NO for medical purposes.

Nitrosating reagents from calixarenes and NO₂

Calixarene-nitrosonium complexes may release NO⁺ and thus act as nitrosating agents. In organic chemistry, nitrosation holds a special place. Alkyl nitrites, nitrosamines/amides, and nitrosothiols are used in biomedicine as NO-releasing drugs.¹² In total synthesis and methodology, –N=O is an important activating group, allowing elegant transformations of amides to carboxylic acids and their derivatives.¹³ In addition, nitrosation mimics interactions between biological tissues and environmentally toxic NO_x gases.³ We discovered, that secondary amides **6** reacted with complexes **7**, with remarkable selectivity (Fig. 6).^{7,8} Chemical properties of the encapsulated NO⁺ are *different* from those in bulk solution and controlled by the cavity.

The cavity in complex **7** protects highly reactive NO⁺ species from the bulk environment. Indeed, complex **7** is quite stable towards moisture and oxygen, and can be handled, for at least several days, without dry box conditions and/or N₂ atmosphere. On the other hand, it can be decomposed within few minutes by addition of larger quantities of H₂O or alcohols, recovering the corresponding free calixarene.

Complex **7** acts as a mild nitrosating reagent.⁸ When added to the equimolar solution of amide Alk'C(O)NHAlk **6** in freshly distilled CHCl₃, it reacted quickly at room temperature, yielding *N*-nitrosamides **8** in 50–95 % (Fig. 6). Dark-blue solutions of **7** discharged upon addition of amide substrates, which is a reasonable *visual test* for the reaction. In the ¹H NMR spectra of the reaction mixtures, signals for amides **6** and complex **7** disappeared and characteristic signals for *N*-nitrosamides **8** and for the nitrosonium-free calixarene were detected.

In reaction with variety of amides **6**, only those possessing *N*-CH₃ substituents were transformed to the corresponding *N*-nitrosamides **8**. No reaction occurred for substrates possessing *N*-Alk groups, bulkier than CH₃. As a consequence, no color discharge was observed for these reaction mixtures.

Tight but reversible encapsulation of NO⁺ species thus offers size-shape selectivities, previously unknown for existing, more aggressive nitrosating agents.¹³ NO⁺, generated from NO⁺-salts, N₂O₃, NO₂/N₂O₄, NO/O₂, HNO₂, etc., is typically not selective. Mechanistically, nitrosation of secondary amides incorporates an electrophilic attack of NO⁺ on a nucleophilic carbonyl oxygen of the substrate, yielding the corresponding *O*-nitroso species.^{14,15} Rapid deprotonation, rotation around the C–O bond and inversion through the nitrogen results in the intermediate, in which, both, the nitrogen lone pair and the NO group are properly oriented for the isomerization to the *N*-nitrosamide. Dimensions and shapes of Alk and Alk' become very crucial when encapsulated reagent **7** is employed. The molecules **6** approach the cavity **7** facing it with the carbonyl oxygen (Fig. 6). This places the *N*-Alk alkyl group in a close proximity to the calixarene two *t*-Bu and two O(CH₂)₅CH₃ groups. For sizeable Alk, this situation could be sterically unfavorable, so that the substrate C=O and the encapsulated NO⁺ would not reach each other. Once formed, the *O*-nitroso intermediate leaves the interior and further collapses in bulk solution, as expected.¹⁵ Due to 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. Otherwise, all reactions should proceed with the roughly same rate, and no selectivity should be seen.

Toward synthetic nanotubes

Recent studies have revealed that gases can be stored inside single-walled carbon nanotubes (SWNTs). This is important. Entrapping isotopes of noble gases by SWNTs may improve their use in medical imaging, where it is desirable to physically confine the gas before injection.¹⁶ SWNTs en-

capsulate N₂, O₂, NO, and CF₄.¹⁷ They have been shown to effectively detect O₂, NH₃, and NO₂.¹⁸ Upon exposure to gaseous molecules the electrical resistance of SWNTs dramatically changes. Storage of H₂ in SWNTs is extremely promising in the design of energy-rich fuel-cell electric devices.¹⁹ Synthetic nanotubes are very rare,²⁰ and their chemistry with gases is not known. This is surprising. Organic synthesis permits much greater structural variations and control over the tube length/diameter, which is important for the gas dynamics and for the design of potential gas storing chambers and conversion/catalytic vessels. We recently designed synthetic tubes for NO₂/N₂O₄ fixation, which is based on calixarenes (Fig. 7, Fig. 8).²¹

In the design, several calix[4]arenes are rigidly connected from both sides of their rims, with at least two symmetrical bridging units. This is structurally possible for a 1,3-alternate conformation. Two pairs of phenolic oxygens are oriented in opposite directions, providing with the diverse route to enhance the tube length modularly. Molecule **9** is a shortest tube, designed to entrap two NO⁺, one per each cavity. It possesses the inner tunnel of ~ 0.5 × 1.1 nm (~ 5 × 11 Å) dimensions and thus represent a first generation of calixarene nanotubes for NO₂/N₂O₄ fixation and conversion. Two 1,3-alternate calix[4]arenes in **9** are connected via their phenolic oxygens through two diethylene glycol bridges (Fig. 7). By our calculations, the bridge length is quite 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.

Exposure of **9** to NO₂/N₂O₄ in chlorinated solvents results in the rapid encapsulation of nitrosonium (NO⁺) cations within its interior. Mono- and dinitrosonium complexes **10** and **11**, respectively, were isolated and characterized by UV-Vis, FTIR and ¹H NMR spectroscopies, and also molecular modeling. The NO⁺ entrapment process is reversible, and addition of water quickly recovered starting tube **9**. Similar to simple complexes **3**, **4** and **7**, encapsulated within the tube NO⁺ species act as nitrosating agents for secondary amides.²¹

Synthesis of longer, polycalixarene-containing nanotubes is on the way (Fig. 8). Such nanotubes may be used for NO₂/N₂O₄ conversion, nitrosonium storage, and act as encapsulated nitrosating reagents. There is also a potential sensory application, since dramatic color changes are involved. Finally, in contrast to cavitands, carcerands, and capsules, supramolecular chemistry of synthetic nanotubes is unexplored.

Conclusions and outlook

Supramolecular chemistry of environmentally and industrially important gases is quickly emerging,²² and now novel sensing and fixation processes for NO₂ are available. These employ simple calix[4]arenes. Calixarenes conveniently transmit the information about NO₂ binding via visible light signals. The described charge-transfer interactions are chemically unique for NO₂ and thus guaranty its detection in the presence of such gases as H₂O, O₂, HCl, SO_x, NH₃, and even NO. For these and other applications, solid-supported calixarene materials were prepared. Synthetic nanotubes were also synthesized for chemical entrapment and conversion of NO₂/N₂O₄. Nitrosonium complexes of calixarenes and based on them nanotubes can be used as vehicles for nitrosonium transfer and encapsulated nitrosating reagents for synthetic methodology. These findings open wider possibilities towards more sophisticated NO₂/NO_x sensing and storing materials.

ACKNOWLEDGMENT

Financial support is acknowledged from the Texas Advanced Technology Program. I also thank members of my research group Dr. G. V. Zyryanov, Yanlong Kang, Dr. Alex V. Leontiev, Voltaire G. Organo, and Stephen P. Stampp for their most valuable contribution to this project.

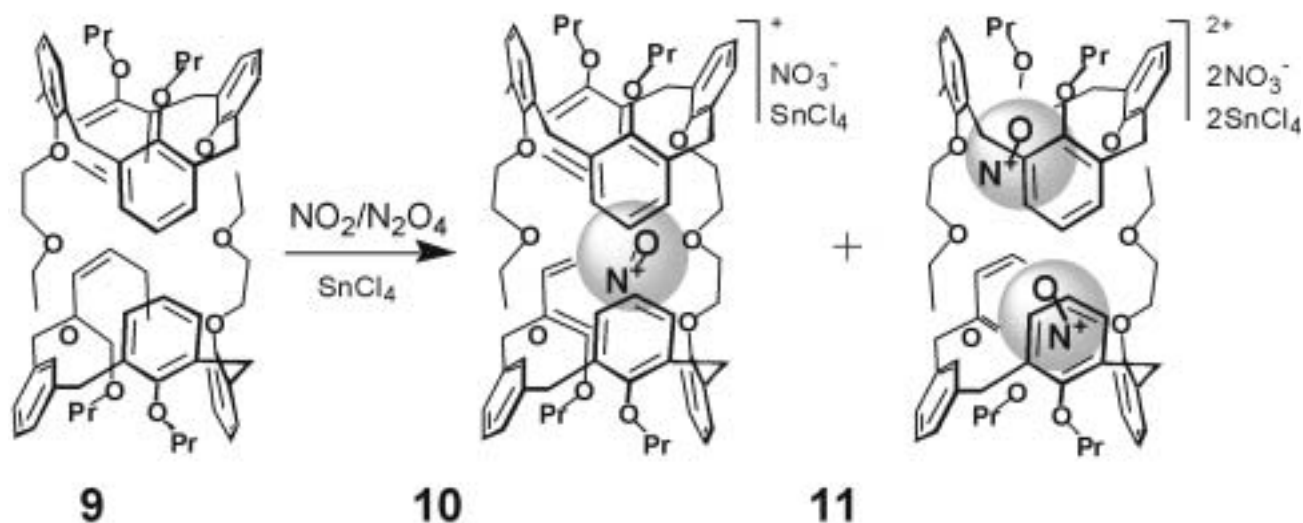


Fig. 7 – Calix[4]arene based tube **9** reacts with NO₂/N₂O₄ with the formation of complexes **10** and **11**. Multiple-guest complexes are expected with the tube elongation.

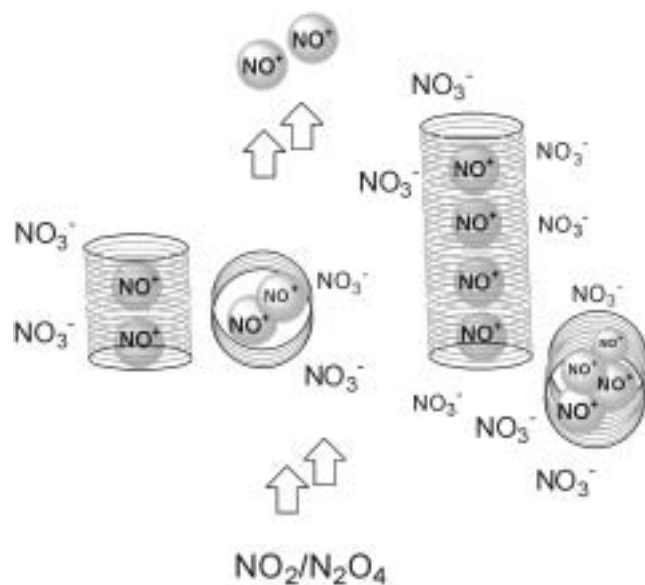


Fig. 8 – Molecular tubes for NO₂/N₂O₄ fixation, a schematic representation. Upon exposure to polyaromatic surfaces of the tubes, N₂O₄ disproportionate to NO⁺NO₃⁻. Nanotubes encapsulate NO⁺ within their interiors. In and out exchange of trapped NO⁺ species is possible, and this can be applied for nitrosation reactions.

References

- U. S. EPA publications: <http://www.epa.gov/air/urbanair/nox/index.html>.
- M. T. Lerda, J. W. Munger, D. J. Jacob, *Science* **289** (2000) 2291.
- (a) S. S. Mirvish, *Cancer Letters* **93** (1995) 17. (b) M. Kirsch, H.-G. Korth, R. Sustmann, H. de Groot, *Biol. Chem.* **383** (2002) 389. (c) D. Hoffman, I. Hoffman, K. El-Bayoumy, *Chem. Res. Toxicol.* **14** (2001), 767. (d) S. Pfeiffer, B. Mayer, B. Hemmens, *Angew. Chem. Int. Ed.* **38** (1999) 1714. (e) A. R. Butler, D. L. H. Williams, *Chem. Soc. Rev.* (1993) 233. (f) S. Tamir, S. Burney, S. R. Tannenbaum, *Chem. Res. Toxicol.* **9** (1996) 821.
- (a) Calixarene 2001; Eds.: Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens; Kluwer Academic Publishers, Dordrecht, 2001. (b) C. D. Gutsche, *Calixarenes Revisited*; Royal Society of Chemistry: Cambridge, 1998. (c) D. M. Rudkevich, *Bull. Chem. Soc. Jpn.* **75** (2002) 393.
- (a) C. C. Addison, *Chem. Rev.* **80** (1980) 21. (b) E. Bosch, J. K. Kochi, *J. Org. Chem.* **59** (1994) 3314.
- G. V. Zyryanov, Y. Kang, S. P. Stamp, D. M. Rudkevich, *Chem. Commun.* (2002) 2792.
- G. V. Zyryanov, Y. Kang, D. M. Rudkevich, *J. Am. Chem. Soc.* **125** (2003) 2997.
- G. V. Zyryanov, D. M. Rudkevich, *Org. Lett.* **5** (2003) 1253.
- Kochi and co-workers obtained similar calix[4]arene-NO⁺ complexes from either NO⁺SbCl₆⁻ and free calixarene or NO gas and the calixarene cation-radical, see: R. Rathore, S. V. Lindeman, K. S. S. Rao, D. Sun, J. K. Kochi, *Angew. Chem. Int. Ed.* **39** (2000) 2123.
- (a) D. Filippini, M. Rösch, R. Aragón, U. Weimar, *Sensors & Actuators B* **81** (2001) 83. (b) H. Steffes, C. Imawan, F. Solzbacher, E. Obermeier, *Sensors & Actuators B* **78** (2001) 106. (c) C. Pijolat, C. Pupier, M. Sauvan, G. Tournier, R. Lalauze, *Sensors & Actuators B* **59** (1999) 195. (d) M. Law, H. Kind, B. Messer, F. Kim, P. Yang, *Angew. Chem. Int. Ed.* **41** (2002) 2405.
- (a) A. Bradford, P. L. Drake, O. Worsfold, I. R. Peterson, D. J. Walton, G. J. Price, *Phys. Chem. Chem. Phys.* **3** (2001) 1750. (b) C. M. Dooling, O. Worsfold, T. H. Richardson, R. Tregoning, M. O. Vysotsky, C. A. Hunter, K. Kato, K. Shinbo, F. Kaneko, *J. Mater. Chem.* **11** (2001) 392. (c) F. Baldini, A. Capobianchi, A. Falai, A. A. Mencaglia, G. Pennesi, *Sensors & Actuators B* **74** (2001) 12. (d) T. Nezel, A. Fakler, G. Zhylyak, G. J. Mohr, U. E. Spichiger-Keller, *Sensors & Actuators B* **70** (2000) 165. (e) S. Capone, S. Mongelli, R. Rella, P. Siciliano, L. Valli, *Langmuir* **15** (1999) 1748. (f) T. Tanaka, T. Ohyama, Y. Y. Maruo, T. Hayashi, *Sensors & Actuators B* **47** (1998) 65. (g) W. P. Hu, Y. Q. Liu, S. G. Liu, S. Q. Zhou, D. B. Zhu, *Supramolecular Science* **5** (1998) 507.
- (a) P. G. Wang, M. Xian, X. Tang, X. Wu, Z. Wen, T. Cai, A. J. Janczuk, *Chem. Rev.* **102** (2002) 1091. (b) V. G. Granik, N. B. Grigor'ev, *Russ. Chem. Bull. Int. Ed.* **51** (2002) 1375.
- (a) E. H. White, *J. Am. Chem. Soc.* **77** (1955) 6008, 6014. (b) G. A. Olah, J. A. Olah, *J. Org. Chem.* **30** (1965) 2386. (c) N. Nikolaidis, B. Ganem, *Tetrahedron Lett.* **31** (1990) 1113. (d) Y. H. Kim, K. Kim, Y. J. Park, *Tetrahedron Lett.* **31** (1990) 3893. (e) D. T. Glatzhofer, R. R. Roy, K. N. Cossey, *Org. Lett.* **4** (2002) 2349. (f) J. Garcia, J. Vilarassa, *Tetrahedron Lett.* **23** (1982) 1127. (g) R. Berenguer, J. Garcia, J. Vilarassa, *Synthesis* (1989) 305. (h) J. E. J. Saavedra, *J. Org. Chem.* **44** (1979) 860. (i) N. Nikolaidis, A. G. Godfrey, B. Ganem, *Tetrahedron Lett.* **31** (1990) 6009. (j) R. W. Darbeau, E. H. White, *J. Org. Chem.* **65** (2000) 1121. (k) F. Wudl, T. B. K. Lee, *J. Am. Chem. Soc.* **93** (1971) 271. (l) J. Garcia, J. Gonzalez, R. Segura, J. Vilarassa, *Tetrahedron* **40** (1984) 3121. (m) J. Garcia, J. Gonzalez, R. Segura, F. Urpi, J. Vilarassa, *J. Org. Chem.* **49** (1984) 3322. (n) T. R. Kelly, W. Xu, Z. Ma, Q. Li, V. Bhushan, *J. Am. Chem. Soc.* **115** (1993) 5843. (o) T. R. Kelly, C. T. Jagoe, Q. Li, *J. Am. Chem. Soc.* **111** (1989) 4522. (p) D. S. Karanewsky, M. F. Malley, *J. Z. Gougoutas, J. Org. Chem.* **56** (1991) 3744. (q) D. A. Evans, P. H. Carter, C. J. Dinsmore, J. C. Barrow, J. L. Katz, D. W. Kung, *Tetrahedron Lett.* **38** (1997) 4535. (r) F. X. Webster, J. G. Millar, R. M. Silverstein, *Tetrahedron Lett.* **27** (1986) 4941. (s) M. Uskokovic, J. Gutzwiller, T. Henderson, *J. Am. Chem. Soc.* **92** (1970) 203.
- R. W. Darbeau, R. S. Pease, E. V. Perez, *J. Org. Chem.* **67** (2002) 2942.
- D. M. Birney, *Org. Lett.* **6** (2004) 851.
- G. E. Gadd, M. Blackford, S. Moricca, N. Webb, P. J. Evans, A. M. Smith, G. Jacobsen, S. Leung, A. Day, Q. Hua, *Science* **277** (1997) 933.
- (a) O. Byl, P. Kondratyuk, S. T. Forth, S. A. FitzGerald, L. Chen, J. K. Johnson, J. T. Yates, Jr., *J. Am. Chem. Soc.* **125** (2003) 5889. (b) O. Byl, P. Kondratyuk, J. T. Yates, Jr., *J. Phys. Chem. B* **107** (2003) 4277. (c) A. Fujiwara, K. Ishii, H. Suematsu, H. Kataura, Y. Maniwa, S. Suzuki, Y. Achiba, *Chem. Phys. Lett.* **336** (2001) 205.
- (a) J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, *Science* **287** (2000) 622. (b) P. G. Collins, K. Bradley, M. Ishigami, A. Zettl, *Science* **287** (2000) 1801. (c) S. Peng, K. Cho, *Nanotechnology* **11** (2000) 57.
- (a) A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, M. J. Heben, *Nature* **386** (1997) 377. (b) C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, M. S. Dresselhaus, *Science* **286** (1999) 1127. (c) W.-F. Du, L. Wilson, J. Ripmeester, R. Dutrisac, B. Simard, S. Denommee, *Nano Lett.* **2** (2002) 343. (d) M. Volpe, F. Cleri, *Chem. Phys. Lett.* **371** (2003) 476.
- (a) A. Ikeda, S. Shinkai, *Chem. Commun.* (1994) 2375. (b) A. Ikeda, M. Kawaguchi, S. Shinkai, *Anal. Quim. Int. Ed.* **93** (1997) 408. (c) S. K. Kim, W. Sim, J. Vicens, J. S. Kim, *Tetrahedron Lett.* **44** (2003) 805. (d) A. Harada, J. Li, M. Kamachi, *Nature* **364** (1993) 516. (e) D. T. Bong, T. D. Clark, J. R. Granja, M. R. Ghadiri, *Angew. Chem. Int. Ed.* **40** (2001) 988.
- G. V. Zyryanov, D. M. Rudkevich, *J. Am. Chem. Soc.* **126** (2004) 4264.
- D. M. Rudkevich, *Angew. Chem. Int. Ed.* **43** (2004) 558.

SAŽETAK

Prepoznavanje i fiksacija NO₂ pomoću kaliksarena*D. M. Rudkevich*

U ovom kratkom prikazu opisan je pristup vizualnoj detekciji, pretvorbi i upotrebi NO₂, što obuhvaća metode i tehnike supramolekularne kemije i upotrebu kaliks[4]arena. Izlaganje alkiliranih kaliks[4]arena djelovanju NO₂/N₂O₄ i u kloriranom otapalu i u čvrstom stanju dovodi do stvaranja duboko obojenih kaliksaren-nitrozonijskih (NO⁺) kompleksa. Utvrđeno je da je NO⁺ smješten unutar kaliksarenih šupljina, a stabilni kompleks s prijenosom naboja rezultirao je s $K_{\text{asoc}} > 10^6 \text{ dm}^3 \text{ mol}^{-1}$ (CDCl₃). Proces nastajanja kompleksa je reverzibilan, pa dodatkom vode i alkohola kompleks disocira, ponovo stvarajući polazne kaliksarene. Prikazano je vezanje kaliks[4]arena na silikagel, što je omogućilo čvrst materijal za vizualnu detekciju i hvatanje NO₂/N₂O₄. Predložen je dizajn i sinteza nanocijevi za hvatanje NO₂/N₂O₄. Pokazana je kemijska primjena NO₂/N₂O₄ kroz prevođenje u kaliksaren-NO⁺ komplekse i njihova upotreba kao nitrozonijskih spremnika i kao prijenosnih reagensa za organske sinteze. Ti pronalasci otvaraju široke perspektive za prepoznavanje NO₂/NO_x, čuvanje i pretvorbu materijala.

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

*Prispjelo 9. ožujka 2004.
Prihvaćeno 17. svibnja 2004.*