CALIX[4]ARENE-BASED SYNTHETIC NANOTUBES

by

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ABSTRACT

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Nanoscale science and technology represents a tremendous opportunity to gain unprecedented insight into the unique phenomena that exists at the nanometer scale, and to use that knowledge to develop materials and devices with novel characteristics. This dissertation explores the unique properties of calix[4]arene-based synthetic nanotubes, the process of filling and characteristics of materials confined in one dimension.

Chapter 1 provides an overview of recently developed nanoscale materials, particularly single-walled carbon nanotubes and their ability to encapsulate materials in a one-dimensional configuration. Molecules inside carbon nanotubes are reported to
exhibit structural and dynamic properties that are not observed in the bulk. Approaches are also discussed towards synthetic nanotubes as a supplement to carbon nanotubes.

Chapter 2 deals with calix[4]arenes as building blocks for constructing nanotubes. Multiple calix[4]arenes in the 1,3-alternate conformation are covalently connected to build robust synthetic nanotubes using conventional organic chemistry protocols. The dimensions of the nanotubes are controlled precisely and easily. They effectively pack into infinite tubular bundles in the solid state.

In Chapter 3, the calix[4]arene-based nanotubes are filled with multiple NO\(^+\) guests. They exhibit typical properties of calix[4]arene-NO\(^+\) complexes as evidenced by UV-vis, \(^1\)H NMR and FTIR spectroscopy. The stoichiometry of the complexes reveals the encapsulation of one NO\(^+\) guest per calixarene cavity. NO\(^+\) guests are entrapped deep inside the nanotube tunnel and experience strong electron donor-acceptor interactions.

In Chapter 4, the dynamics of the filling material inside calix[4]arene nanotubes are discussed. The tunnel of the nanotube allows the NO\(^+\) guests to freely rotate along the N-O axis and also tumble within the cavity at room temperature. Though the filled nanotube is stable, it allows the release and re-entry of guests within its hollow structure. NO\(^+\) can be transferred to and from another host such as 18-crown-6. The guest exchange and dynamics are monitored by conventional spectroscopic techniques.
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CHAPTER 1
INTRODUCTION

1.1 Importance of Nanoscale Science and Technology

Nanoscale science and technology (NS&T) is a rapidly developing field. It deals with the design, construction, and utilization of functional materials, devices and systems in the range of about 1 to 100 nanometers (nm).\(^1\) Such materials are of great interest because they display properties significantly different from those displayed by either atoms or bulk materials.\(^2\) The capability to manipulate matter at this scale can therefore lead to novel and improved characteristics and behavior of materials.

Figure 1. Current and potential applications of nanoscale science and technology.\(^1\)
Applications of NS&T span across the fields of science, engineering, technology and medicine (Figure 1). Early applications of nanoscale materials involve nanoscale powders like titanium dioxide and zinc oxide used by the cosmetics industry for facial creams and sunscreen lotions.\(^1\) Titanium dioxide powders are also used in paints to improve its reflective properties; and in wear-resistant coatings.\(^3\) Nanoparticles are widely used in the electronics industry for the manufacture of integrated circuit chips and hard disks.\(^4\) In the biomedical field, nano-sized structures called liposomes have been synthesized for improved delivery of therapeutic agents, while others have developed fluorescent nanoparticles to detect tumor cells, or infectious and genetic diseases.\(^5\) Further developing technologies in NS&T involve more efficient catalysts for industrial processes and waste treatment,\(^6\) sensors for chemical and biological hazard detection, and environmental monitoring,\(^7\) fuel cells,\(^8\) and improved materials for implants and artificial organs.\(^9\)

In the United States, the potential impact of NS&T on economics has led to the establishment of the National Nanotechnology Initiative (NNI), which aims to accelerate the discovery, development, and deployment of nanotechnology. Financial support for nanotechnology research and development has now reached over $5 billion since its inception in 2001.\(^2\) This tremendous support is an indication of the growing interest in advancement of this multi-disciplinary field.

Indeed, the ability to understand and control matter on the nanoscale can open new opportunities for technological and commercial development.
1.2 Nanotubes

Among the nanostructured materials being studied extensively are nanotubes. In Nature, hollow tubular structures perform diverse functions such as selective transport of molecules and ions across membranes, and catalysis.\(^{10}\) These biological structures have inspired researchers to construct nanotubes for sensing, transport, catalysis, storage, and other applications.\(^{10-12}\) Another goal of constructing nanotubes, which goes beyond mimicking biological functions, is to confine materials in a quasi-one dimensional system which may lead to novel properties.\(^{13}\)

1.2.1 Carbon Nanotubes

Carbon nanotubes can be thought to consist of graphitic sheets which have been rolled up into a cylindrical shape. Since their discovery by Iijima\(^ {14}\) and by Bethune et al.\(^ {15}\) in 1993, there has been a large interest in the study of single-walled carbon nanotubes (SWNTs), particularly in filling them with foreign guests. Aside from the discovery or preparation of novel materials, the interest in SWNTs lies in the peculiar properties that can be expected from the nanometer dimensions associated with the filling process. As mentioned earlier, physical features can be drastically modified for nanoscale materials. This is especially true for SWNTs, which have inner hollow cavities with diameters ranging from 1 to 20 nm.\(^ {16}\) Their narrow channel forces the filling materials to adopt a one-dimensional morphology. In this case, SWNTs can either serve as molds or composite materials for preparing nanoscale wires, transistors and sensors. SWNTs can also serve as containers for nano-sized catalysts. In this instance, the inert carbon sheath protects the catalyst from the components of a catalytic
process. Upon oxidation, the carbon is removed and the catalyst becomes activated.\textsuperscript{17} Similarly, SWNTs can also be used to encapsulate important gases like hydrogen for fuel storage.\textsuperscript{18}

1.2.1.1. Molecules Inside Single-Walled Carbon Nanotubes

For potential applications, it is valuable to gain insight on the structural and dynamic behavior of guests encapsulated in carbon nanotubes. The first reported molecule inside SWNTs was the buckminster fullerene $C_{60}$ (Figure 2).\textsuperscript{19} These so-called peapods formed spontaneously as by-products during the post-synthesis of the nanotubes. The structural and dynamic behavior of $C_{60}$ in SWNTs has been analyzed by high-resolution transmission electron microscopy (HRTEM).\textsuperscript{20} It was found that the interfullerene spacing, dictated by the van der Waals interaction, is about 3\% shorter in nanotubes than in bulk crystals (1.004 nm). This suggests that fullerenes experience compression inside nanotubes as a result of encapsulation. Also, depending on the internal diameter of the nanotubes, several packing arrangements were found possible for $C_{60}$ inside nanotubes, none of which exist in the bulk.

Figure 2. SWNTs filled with fullerenes. (a) structural representation, (b) HRTEM micrograph image, (c) structural representation of a $C_{60}$ crystal.\textsuperscript{19}
Studies carried out with SWNTs filled with an ellipsoidal fullerene, C$_{70}$, revealed two different orientations inside the nanotube with intermolecular spacing of 1.00 and 1.10 nm for the transverse and longitudinal orientations, respectively (Figure 3a-b). In narrower 1.36 nm nanotubes, the elongated fullerenes adopt exclusively a longitudinal orientation to minimize van der Waals repulsion with the interior of the nanotubes; while in wider 1.49 nm nanotubes, the molecules are oriented in a transverse fashion to maximize the van der Waals attractive forces. These observations suggest that fullerene-nanotube interactions have greater influence than fullerene-fullerene interactions on the molecular orientations in these systems. On the other hand, a phase transition, rather than change in orientation, was observed for C$_{60}$ peapods as a consequence of nanotube diameter (Figure 3c-d). Below 1.45 nm nanotube diameter, the C$_{60}$ molecules form a linear array, while above which they form a zigzag phase. Again, the fullerene-nanotube interaction seems to be the dominant interaction for this phase transition.

Figure 3. Molecular orientations of fullerenes inside SWNTs. (a) longitudinal and (b) transverse orientation of C$_{70}$, (c) straight chain packing and (d) zig-zag packing of C$_{60}$. 

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Another interesting behavior is observed for endohedral metallofullerenes inside SWNTs (Figure 4). Endohedral metallofullerenes are molecules containing one or more metal atoms inside the fullerene cage, denoted here as X@C\textsubscript{n} (where X is an atom and C\textsubscript{n} is the fullerene cage). These molecules possess electric dipole moments resulting from the interaction of the incarcerated metal atom with the cage. The effect of dipole interactions on molecular orientation inside nanotubes was studied with Ce@C\textsubscript{82} molecules. HRTEM images show that the metallofullerenes tend to align their dipole moments along the nanotube axis and maximize dipole-dipole interactions with neighboring molecules. Such an alignment is not observed in the bulk crystal or in solutions of Ce@C\textsubscript{82} where the molecules freely rotate at room temperature.

Figure 4. Endohedral metallofullerenes inside SWNTs. Structural diagram of (a) Ce@C\textsubscript{82}, (b) Ce@C\textsubscript{82} inside SWNTs, (c) HRTEM micrograph of Ce@C\textsubscript{82} in SWNTs.\textsuperscript{21}

Non-fullerene molecules inside SWNTs have been investigated as well. These molecules have also shown to exhibit peculiar properties. For example, octasiloxane (Si\textsubscript{8}H\textsubscript{8}O\textsubscript{12}), a cube-shaped molecule with an H-atom pointing outwards from each
corner of the cube, was inserted in SWNTs with diameters of 1.4 - 1.5 nm and analyzed by IR spectroscopy (Figure 5). Since the H atoms can have direct contact with the nanotube surface, the stretching vibrations of Si – H bonds were used to probe the interaction between the octasiloxane and the nanotube. The vibrational frequency of the Si – H bond, which normally appears as a sharp band at $\nu = 2277 \text{ cm}^{-1}$ in CCl$_4$ solution, was found broadened and red-shifted by about $\Delta \nu = -15 \text{ cm}^{-1}$. This is in contrast to a $\Delta \nu = +17 \text{ cm}^{-1}$ shift in Si – H absorption band observed for octasiloxane in solid state. This observation suggests that the Si – H bonds elongate as a result of dispersion forces acting between Si$_8$H$_8$O$_{12}$ and the nanotube.

![Structural representations of (a) Si$_8$H$_8$O$_{12}$, (b) Si$_8$H$_8$O$_{12}$ inside SWNTs.](image)

Figure 5. Octasiloxane in SWNTs. Structural representations of (a) Si$_8$H$_8$O$_{12}$, (b)-(c) Si$_8$H$_8$O$_{12}$ inside SWNTs.  

On the other hand, inserting Si$_8$H$_8$O$_{12}$ in narrower nanotubes (diameters of 0.8-1.2 nm) resulted in a red shift of the Si – H vibrational frequency by only $\Delta \nu = -6 \text{ cm}^{-1}$. This indicates that, in addition to van der Waals dispersive forces, the molecules in
narrower nanotubes experience greater compression than in wider nanotubes. Such a compression would shorten the Si – H bonds and effectively compensate for the elongation due to the dispersion interactions and thus suppress the observed red shift of the v(Si-H) band.

![Figure 6](image)

Figure 6. Polymerization of fullerene epoxide in (a) solid state and (b) inside SWNTs.\textsuperscript{23}

The encapsulation effect has also been demonstrated in the polymerization of fullerene epoxide, C\textsubscript{60}O confined inside SWNTs.\textsuperscript{23} Fullerene epoxide is stable at room temperature. Above 200°C, the strained epoxide ring opens up, forming a reactive intermediate, and reacts with carbon-carbon double bonds to form a furan ring. Polymerization of C\textsubscript{60}O in the solid state produces tangled, branched, three-dimensional polymers (Figure 6a). On the other hand, C\textsubscript{60}O inside SWNTs result in linear, unbranched polymers. The C\textsubscript{60}O molecules bond to each other in a head-to-tail fashion, indicating that the molecules were aligned in the same direction during reaction (Figure 6b).
The confinement of water molecules inside carbon nanotubes has been studied by vibrational spectroscopy.\textsuperscript{24} In an infinite ice crystal each water molecule is tetrahedrally coordinated, donating and accepting two hydrogen atoms simultaneously to form a hydrogen-bonded network. This arrangement is disrupted in agglomerates of crystalline water in finite sizes, resulting in a variety of shapes for small water clusters with different types of OH groups ranging from bulk-like to free OH groups. The diversity of the OH groups can be detected by vibrational spectroscopy.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{water_in_cot.png}
\caption{Snapshot from a molecular simulation of water inside a SWNT forming heptagon rings. (A) End view and (B) side view. (Red = oxygen, blue = hydrogens involved in inter-ring H-bonding, green = hydrogens involved in intra-ring H-bonding.\textsuperscript{24}}
\end{figure}

It was found that H$_2$O molecules confined inside SWNTs form stacked ring structures that involve hydrogen bonds of two types, as illustrated in Figure 7. Hydrogen bonds formed within the ring structure exhibit frequencies similar to bulk H$_2$O (ν(OH) = ~3400-3450 cm$^{-1}$) while hydrogen bonds formed between neighboring rings exhibit a distinct OH stretching frequency. The infrared mode at ν = 3693 cm$^{-1}$ assigned to the “free” OH groups dangling at the surface of amorphous ice disappears
when water diffuses inside the nanotube, and an OH vibration mode at $\nu = 3507 \text{ cm}^{-1}$ was observed in addition to associated OH features in the $\nu = 3000-3450 \text{ cm}^{-1}$ region. The observed infrared mode at $\nu = 3507 \text{ cm}^{-1}$ is assigned to vibrations of the inter-ring OH groups, and believed to be a direct result of the confinement of H$_2$O molecules in SWNTs.

1.2.1.2. Experimental Difficulties Associated with Carbon Nanotubes

In spite of a number of publications devoted to the study and use of carbon nanotubes, there are several difficulties associated with them. One of the primary challenges encountered involves purity. SWNTs are usually prepared by dissolving carbon in a transition metal nanoparticle melt then subjecting the mixture to high temperature.\textsuperscript{25} This process produces carbon nanotubes contaminated with metal catalysts, amorphous carbon and non-SWNT carbon particles. Several purification methods have been introduced and these usually involve filtration to remove large graphite particles, treatment with concentrated acid or oxidants to destroy the catalysts, and chromatography.\textsuperscript{26} However, these methods are usually difficult to scale up in order to obtain large volumes of sample. Moreover, treating the sample under strong oxidizing conditions tends to destroy the sample.

The synthesis of carbon nanotubes normally produces closed structures which prevent access to its interior.\textsuperscript{27} Chemical treatment is therefore required to open the end caps to access the interior of the nanotube. This is usually done using strong oxidizing agents. Again, this procedure can damage the nanotubes and introduce several defect sites on its walls.
Another limitation that hampers the practical use of SWNTs is the lack of solubility and the difficulty of manipulation in any solvent. They can be dispersed in some solvents by sonication but only temporarily. To address this issue, functional groups are introduced on the surface of the carbon nanotubes; typically by taking advantage of defect sites created by oxidation treatment.\textsuperscript{28,29}

Finally, the investigation involving filled SWNTs and understanding its mechanism is non-trivial.\textsuperscript{16,30,31} The use of nano-probe spectroscopic methods on isolated, single SWNTs is required to conduct accurate measurements, and ascertain whether foreign guests are encapsulated in the tube and not intercalated between tubes. Methods such as high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy or electron energy loss spectroscopy (EELS) have to be used for accurate characterization.\textsuperscript{32}

These challenges should therefore be addressed before SWNTs can have viable applications. In the meantime, researchers have also considered looking for other means to construct nanotubes.

1.2.2 Synthetic Nanotubes

Aside from carbon, inorganic and organic systems have been introduced to synthesize nanotubes. Although inorganic systems benefit from the majority of elements in the periodic table, organic systems take advantage of its inherent power of synthetic molecular and supramolecular chemistry.\textsuperscript{33} Organic synthesis also provides greater structural variation and control over the diameter and length of the tube. These features are important for studying guest dynamics and in the design for potential
storing chambers and catalytic vessels. Thus, the development of a design which is analogous to carbon nanotubes may hold promise in understanding the principles of supramolecular chemistry, particularly multiple guest encapsulation, chemical dynamics and information storage/processing.

1.2.2.1 Self-assembled Synthetic Nanotubes

A novel class of self-assembling nanotubes has been introduced by Ghadiri and co-workers.\textsuperscript{10} These are based on cyclic peptide molecules consisting of even numbered alternating D- and L-amino acids. They showed that these molecules self-assemble via hydrogen bonding into nanotubes (Scheme 1).

![Scheme 1. Schematic diagram of nanotube self-assembly from cyclic D, L-peptides.\textsuperscript{10}](image)

An interesting feature of this peptide nanotube is the ease with which the external surface properties and the internal diameter of the tube may be altered by changing the appropriate amino acid side chains and the size of the peptide ring, respectively. For example, they have shown that with appropriate hydrophobic side
chains, these cyclic peptides partition into nonpolar lipid bilayers and self-assemble to form artificial transmembrane ion channels. Similar systems have also been utilized as biosensors for detection of ions and small organic molecules. On the other hand, Gazit and Reches $^{34}$ used a cyclic phenylalanine structural motif to build nanotubes and encapsulate silver ions in solution. Reduction of the ionic silver within the tubes, followed by degradation of the peptide backbone, resulted in the formation of silver nanowires.

![Scheme 2. Self-assembly of rosette nanotubes. (A) bicyclic base system (B) Molecular model of the rosette structure (C) Molecular model of the proposed nanotube.][13]

Another self-assembled nanotube was reported by Fenniri et al. $^{36}$ The design is based on a heteroaromatic bicyclic base motif. These molecules self-assemble into discrete nanotubular structures in water. With the unique feature of forming Watson-Crick type H-bonding arrays, plus its hydrophobic character, the bicyclic system undergoes a hierarchical self-assembly to form six-membered rosettes. Several stacks of these rosettes then organize together to grow hollow tubular structures with an open

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channel 1.1 nm across and several micrometers long (Scheme 2). Varying the functional groups introduced to the bicyclic motif modifies the surface properties of the nanotubes, and consequently influences its structure, stability and functionality.\textsuperscript{33,35}

Another design introduced by Matile and co-workers\textsuperscript{37} was based on rigid-rod \(\beta\)-barrels. These artificial \(\beta\)-barrels are synthesized by coupling the N-termini of short peptide strands with the carboxylic acids along the scaffold of octa(\(p\)-phenylene)s. Self-assembly of the octa(\(p\)-phenylene)-peptide conjugate results in the formation of the rigid-rod \(\beta\)-barrels via hydrogen bonding (Scheme 3). The barrels then serve as synthetic ion channels or pores when affixed in planar or spherical lipid bilayers.

![Scheme 3. Formation of rigid-rod \(\beta\)-barrels from octa(\(p\)-phenylene)s. Arrows between octa(\(p\)-phenylene) staves indicate \(\beta\)-sheets (N \(\rightarrow\) C).\textsuperscript{37}](image)

The design allows molecules to interact with the barrel either at the external surface or at the pore. Interaction of molecules with the external residues causes an increase in barrel-membrane interaction which leads to the activation or opening of the pore. On the other hand, interactions of molecules that pass through the pore across a
bilayer membrane may result to pore-closing or blockage. Recognition of guests is usually measured by taking advantage of the synthetic pores’ intrinsic fluorescent property. A broad spectrum of recognized guests already studied range from small inorganic ions to higher aromatics such as fullerenes and calixarenes to polypeptides, polysaccharides and DNA.\textsuperscript{11}

Scheme 4. Self-assembled nanotubes through metal coordination.\textsuperscript{38,39}

A novel approach to self-assembled nanotubes was also reported by Fujita and co-workers.\textsuperscript{38} Their approach was based on metal coordination. They found that oligo(3,5-pyridine)s self-assemble into tubular structures with the aid of rod-like molecules acting as templates (Scheme 4). The oligomeric ligand, which takes on a planar conformation due to the dipole-dipole repulsion between pyridine nuclei, is linked together through coordination with Pd(II) building blocks. This process,
however, only occurs in the presence of a template molecule which interacts strongly with the pyridine moieties through $\pi-\pi$ interactions. Thus, when the template molecules are removed, the nanotube collapses into oligomers. However, when the ligand was extended using a biphenyl linker, the longer nanotube formed becomes more stable even after removal of the template molecule.$^{39}$

1.2.2.2 Covalent Strategy

Synthetic nanotubes constructed through self-assembly have shown promise as sensors, catalysts, ion channels, metal wire scaffolds, and drug delivery vehicles.$^{40}$ However, these nanotubes are controlled by non-covalent interactions and are thus, only stable under specific conditions. For example, hydrogen-bond-driven self-assemblies like peptide and rosette nanotubes are sensitive to pH and solvent because the protonation states of amino acid residues influence the strength of intermolecular hydrogen bonding.$^{35,40}$ Another example was presented earlier involving coordination nanotubes by Fujita and co-workers in which the nanotubes are only stable in the presence of a template molecule.$^{38}$ Thus, to stabilize the nanotubes without sacrificing structure and functionality, researchers have introduced the covalent approach.

The combined strategy involving non-covalent interaction and covalent bonding has been demonstrated by Harada and co-workers.$^{41}$ Using threaded $\alpha$-cyclodextrins (CD) as precursors, they successfully constructed the first reported synthetic nanotube.

$\alpha$-CDs are cyclic oligomers of glucose which contain a cylindrical cavity of approximately 0.7 nm in depth and 0.45 nm in diameter. They were found to complex with poly(ethylene glycol) very efficiently, forming a chain of threaded CD complexes
called polyrotaxanes. Bulky stoppers (NH(C₆H₃)(NO₂)₂ groups) were introduced at the ends of the chain, keeping CD molecules in close contact with each other and preventing their dissociation. Upon treatment with epichlorohydrin in aqueous base, the CD hydroxyl groups formed covalent bonds with neighboring units (Scheme 5). Adding a large excess of base then cleaved the stopper groups and subsequently released the CD-based nanotubes in solution.

![Scheme 5](image)

Scheme 5. Preparation of synthetic nanotube from α-cyclodextrins.

The CD nanotubes were reported to encapsulate I₃⁻ ions from a pale yellow solution of potassium iodide with iodine (KI-I₂), resulting in a deep red colored solution. This color change was not observed with monomeric α-CDs nor with
randomly cross-linked α-CDs; thus, possibly indicating the presence of linearly arranged I$_3^-$ ions inside the nanotube.

Biesalski and co-workers$^{42}$ introduced a polymer hybrid version of the cyclic peptide nanotube (Scheme 6). The octameric cyclic peptides with alternating D- and L-configurations were modified with bromoisobutyramide initiators attached on the lysine side chains. Once the nanotubes are formed, these were reacted with N-isopropylacrylamide monomer and subjected to atom-transfer radical polymerization (ATRP) reaction. This technique allowed the polymer to grow a homogeneous shell around the cylindrical peptide core.

Scheme 6. Schematic outline of the synthesis of peptide-polymer hybrid nanotubes.$^{42}$
Hetch and co-workers\textsuperscript{43} generated organic nanotubes from intramolecularly crosslinked, helically folded polymers. They synthesized amphiphilic poly(\(m\)-phenyleneethynylene)s that bear cinnamate groups to serve as backbone. In polar solvents, non-covalent interactions such as \(\pi-\pi\) stacking of the aromatic units and solvophobic interactions allow the polymer strand to fold itself into a helical conformation. Such conformation brings reactive groups in proximity for effective cross-linking via \([2+2]\) photodimerization, producing rigid organic nanotubes (Scheme 7). The helix-coil transition can be monitored using UV-vis absorption and fluorescence spectrosopies. However, the degree of cross-linking was only estimated to be about 20-30%.

\begin{center}
\textbf{Scheme 7. Synthesis of crosslinked amphiphilic poly(\(m\)-phenyleneethynylene).}\textsuperscript{44}
\end{center}

Another covalent design was introduced by Zimmerman and co-workers.\textsuperscript{45} They incorporated porphyrins and dendrimers in constructing nanostructures. In this case, the porphyrin assembly serves as a core-shell for molding dendrimers around it (Scheme 8). Porphyrin dendrimers containing multiple alkene end groups were first synthesized then complexed with tin (IV). The metalloporphyrin dendrimers were bridged together, forming stacks of the dendrimers. The peripheral alkene groups were then subjected to
ring-closing metathesis (RCM) to generate the nanotubes. Finally, in order to form hollow structures, the porphyrin moiety was removed at the dendron-porphyrin linkages by transesterification reaction. With this strategy, the thickness of the tube wall is determined by the generation of the dendron, and the inner diameter can be controlled by an appropriate sized core. Functionality of the outer and inner surfaces of the tube can also be modified by linking desired reactive groups. However, there is no significant control over the length of the tube. Also, more information is required to determine whether the hollow structure collapses or remains open upon removal of the porphyrin core.

Scheme 8. Synthesis of nanotubes from porphyrin dendrimers.45
1.3. Summary

In summary, the fast-growing field of nanoscale science and technology has led to important discoveries and potential applications. One such discovery is carbon nanotubes; particularly, single-walled carbon nanotubes. These nanotubes have a unique structure with the ability to encapsulate materials in a one-dimensional configuration. Such a property has motivated researchers to investigate the effect of confinement to the filling materials. Several reports have shown that molecules inside carbon nanotubes exhibit structural and dynamic properties that are not observed in the bulk. However, carbon nanotubes suffer from the high cost of processing, low purity and homogeneity, poor solubility, and lack of simple methodologies for accurate measurements. Alternatively, synthetic nanotubes offer simplicity and convenience in construction, processing and analysis. Several approaches to synthetic nanotubes which utilize covalent and non-covalent interactions have been developed. Still, there are limitations to their design and their ability to encapsulate materials remains a challenge. An improved design with improved encapsulation properties is needed to overcome these drawbacks and further add to our understanding of confined materials at nanoscale dimensions.
CHAPTER 2

CALIX[4]ARENE-BASED SYNTHETIC NANOTUBES

2.1 Calix[4]arenes

Calix[n]arenes are a popular class of macrocycles formed from the condensation of a \( p \)-substituted phenol with formaldehyde. The “n” refers to the number of phenolic residues in the calixarene. The descriptive name “calixarene” was coined by Gutsche because the bowl-shaped conformation of the cyclic tetramer resembles a Greek vase called a *calix crater*.

Calixarenes are characterized by an upper rim, a lower rim and a central annulus (Figure 8). The selective functionalization at the upper and/or lower rim makes calixarenes extremely versatile host frameworks for cations, anions and neutral molecules.

![Diagrams of Calix[4]arenes](image)

**Figure 8.** Representation of calix[4]arenes.
Calix[4]arenes adopt four possible conformations, namely cone, partial cone, 1,2-alternate and 1,3-alternate. These conformations can be described based on the projections of the aryl groups, either upward (“u”) or downward (“d”), relative to the annulus. Thus, “u,u,u,u,” is designated for cone; “u,u,u,d” for partial cone; “u,u,d,d” for 1,2-alternate; and “u,d,u,d” for 1,3-alternate, as illustrated in Figure 9.46

![Figure 9. Conformations of calix[4]arenes.](image)

The four conformations can be identified through their $^1$H and $^{13}$C NMR spectra. The NMR patterns of the bridging methylene groups are very useful in distinguishing three out of the four conformations (Figure 10). The $^1$H NMR spectrum of cone calix[4]arenes with the same substituents at each para position shows a pair of doublets (at ~ 3.1 ppm and 4.0 ppm) for the methylene bridges below the coalescence temperature, while a singlet (at ~3.5 ppm) is observed for the 1,3-alternate conformer. Both pair of doublets and singlet are present in partial cone and 1,2-alternate conformations. Although the less common 1,2-alternate conformation shows a similar
pattern to the partial cone, the two conformations can be distinguished by the number and multiplicity of proton signals in the aromatic region of the spectrum. The conformations also exhibit distinguishing patterns in the $^{13}$C NMR spectrum. De Mendoza and co-workers$^{51}$ have shown that the bridge methylene carbon resonance is near 31 ppm when two adjacent aryl groups are in the syn orientation, and near 37 ppm when they are in the anti orientation.

![Figure 10. Patterns of signals in $^1$H and $^{13}$C NMR of four calix[4]arene conformers.](image)

Among the conformers, calix[4]arenes in the 1,3-alternate conformation have several interesting structural features. They have two metal-binding sites at the edges of the calix[4]arene cavity. The binding sites are composed of two “hard” phenolic oxygens and two “soft” π-basic benzene rings. These two binding sites, defined by two cofacial pairs of aromatic rings that are oriented orthogonally along the cavity axis, are
linked together to form a cylindrical π-basic benzene tunnel. X-ray studies reveal that this tunnel is ~5-6 Å in diameter. These unique structural features are reflected by their metal-binding properties. For example, 1,3-alternate calix[4]arenes can form 1:1 complexes with metal cations like K⁺ and Ag⁺. Moreover, in a 1:1 complex, the metal cation vibrates between the metal-binding sites through the π-basic tunnel (Figure 11).

![Figure 11. Metal-tunneling through a π-basic tube of 1,3-alternate calix[4]arene.](image)

These characteristics of the 1,3-alternate calix[4]arene have led to the construction of synthetic nanotubes based on this motif which can serve as metal cation receptors or artificial ion channels.

### 2.2 Early Calixarene-based Nanotubes

Calix[4]arene-based nanotubes or calix[4]tubes were first introduced by Shinkai and co-workers. Taking a cue from the dynamic behavior of small metal cation complexes with 1,3-alternate calix[4]arenes, they connected several calixarenes to form
nanotubes 5-7b (Figure 12). Conceptually, nanotubes 5-7b would allow metal cations to tunnel through its π-basic interior.

![Diagram of nanotubes 5, 6, 7a, and 7b]

Figure 12. Shinkai’s calix[4]arene nanotubes.57

Complexation experiments with AgCF₃SO₃ has revealed the presence of a 1:1 Ag⁺ ion complex with calix[4]tube 5. Analysis of the ¹H NMR spectrum of the complex suggests that the Ag⁺ ion is delocalized between two calixarenes. The authors proposed that the metal cation oscillates between metal-binding sites in calix[4]tubes in two possible modes: intracalixarene metal-tunneling and intercalixarene metal-hopping.
(Figure 13). This dynamic behavior, however, was not observed in the complexation with calix[4]tube 6; instead, a mixture of free tube 6 and 1:2 tube-Ag$^+$ complex was found in the $^1$H NMR spectum. It was suggested that the $p$-substituents used to connect the two calixarenes interfered with the cation-$\pi$ interaction, thus, suppressing the metal tunneling. In this case, the Ag$^+$ ions were said to be localized at the edges of the tube, interacting with the calixarene phenyl groups and the propyloxy-oxygen groups through cation-$\pi$ and electrostatic O-Ag$^+$ interactions, respectively.

![Diagram](image)

Figure 13. Intracalixarene metal-tunneling (A) and intercalixarene metal-hopping (B). $^{57}$

Similarly, there was no evidence of metal-tunneling in the complexation studies with calix[4]tube 7a (no report of the same experiment with 7b). A 1:1 mixture of 7a and AgO$_3$SCF$_3$ yielded three different species: free 7a, 7a$\cdot$Ag$^+$ and 7a$\cdot$(Ag$^+$)$_2$ in a 1:2:1 ratio. This result implies that Ag$^+$ is bound to 7a according to probability. Moreover, the lack of metal-tunneling was suspected to be the result of several structural features of 7a. These are: the para-substitution of phenyl groups in the calixarene units; the
increased distance between two calixarene units relative to other structures; and the non-ionophoric bridges connecting the calixarene units.

Kim et al.\textsuperscript{58} reported similar multiply-connected 1,3-alternate calix[4]arenes (Figure 14). However, the terminal calixarene units were capped with crown ethers (calix[4]crowns). Similar to Shinkai, metal ion shuttling was not observed, and metal ions were only bound at the end-calixcrown “stoppers.”\textsuperscript{59} X-ray crystal structure of the biscalix[4]crown 8 with K\textsuperscript{+} ions revealed that electrostatic interactions between the oxygen donor atoms of the crown ether ring and the metal cation plays a major role for entrapping the metal ion while the cation-\pi interaction plays a minor role.

Our group recently found cation-\pi complexes with calix[4]arenes which feature unique stabilities. These are based on interactions between calix[4]arenes and nitrosonium (NO\textsuperscript{+}) cations.
2.3 Towards A Novel Design for Synthetic Nanotubes

Our laboratory recently discovered that simple calix[4]arenes, for example 13, reversibly interact with NO₂/N₂O₄ and entrap the highly reactive NO⁺ cation within their π-electron rich interiors (Scheme 9). Molecular modeling suggested that the 1,3-alternate calix[4]arene has a sufficiently wide cavity to accommodate one NO⁺ guest.

NO\(^+\) is generated from \(\text{N}_2\text{O}_4\), which is known to disproportionate to \(\text{NO}^+\text{NO}_3^-\). When \(\text{NO}_2/\text{N}_2\text{O}_4\) gas is bubbled through a \(\text{CHCl}_3\) solution of \(\text{13}\), a deep purple solution was produced instantly. This is in striking contrast to the colorless solution of \(\text{13}\) and a pale yellow solution of \(\text{NO}_2/\text{N}_2\text{O}_4\) in \(\text{CHCl}_3\). Upon complexation, the UV-vis absorption spectrum changed accordingly, with the appearance of a broad band at \(\lambda_{\text{max}} = 512\) nm. This observation is attributed to a strong charge-transfer process between the electron-deficient \(\text{NO}^+\) species and the \(\pi\)-electron rich calixarene cavity, in which the \(\text{NO}^+\) species is sandwiched between two aromatic rings.\(^{62-64}\)

The host-guest dynamics of the \(\text{NO}^+\) complexes can also be studied using \(^1\text{H}\) NMR. The \(^1\text{H}\) NMR spectrum of complex \(\text{14}\) exhibited new sets of signals compared to empty calixarene \(\text{13}\) (Figure 15). The aromatic proton signals of empty \(\text{13}\) were seen as a doublet and a triplet, 2:1, at 6.92 and 6.68 ppm, respectively (\(J = 7.5\) Hz). In the \(\text{NO}^+\) complex \(\text{14}\), these signals were transformed into a triplet and a doublet, 1:2, at 7.17 and 7.08 ppm, respectively (\(J = 7.5\) Hz). The methylene bridge \(\text{CH}_2\) and \(\text{OCH}_2\) protons of \(\text{13}\) were seen as a singlet and a triplet, 1:1, at 3.62 and 3.54 ppm (\(J = 7.5\) Hz), respectively; whereas, in complex \(\text{14}\), these were transformed into a triplet and a singlet, 1:1, at 3.87 and 3.60 ppm, respectively (\(J = 7.5\) Hz). These results show that aside from the \(\text{NO}^+\)-aromatic interaction, the \(\text{NO}^+\) guest also interacts with the phenolic oxygens through ion-dipole interactions.

The stepwise addition of \(\text{NO}_2/\text{N}_2\text{O}_4\) or commercially available \(\text{NO}^+\text{SbF}_6^-\) salt in \(\text{CHCl}_3\) solution reveals both free \(\text{13}\) and complex \(\text{14}\), indicating that the \(\text{NO}^+\) exchange
in and out of the calixarene cavity is slow on the NMR time scale. This observation is typical for host-guest complexes with high association constants ($K_{\text{assoc}} >> 10^6 \text{ M}^{-1}$).

Figure 15. Portions of the $^1$H NMR spectra (500 MHz, CDCl$_3$, 295 K) of (a) calix[4]arene 13, and (b) nitrosonium complex 14.

The complexes formed are very stable and can be stored in the absence of moisture for several weeks, both in CHCl$_3$ solution and in the solid state. On the other hand, the complexation process is reversible, and the NO$^+$ guest can leave the calixarene
cavity. Addition of H₂O or methanol to the freshly prepared CHCl₃ solution of complex 14 resulted in the complete removal of NO⁺ and the recovery of calixarene 13.

2.3.1. Design of Calix[4]tubes

Taking advantage of the unique chemistry between calixarenes and NO⁺ species, in principle calix[4]arene tubes can now be constructed and filled. In order to accomplish this, the calix[4]arenes should be rigidly connected from both sides of their rims, with at least two symmetrical bridging units. This is possible for a 1,3- alternate conformation. The 1,3-alternate calix[4]arenes are connected via their phenolic oxygens through two diethylene glycol bridges. Based on molecular models, the bridge length is optimal, providing a relatively rigid tubular structure with narrow gaps between calixarene modules. By our calculations, the calix[4]arene units are separated by about 9 Å, and the nanotubes have dimensions of about 6 Å in diameter and 15, 25, 35, and 45 Å in length for calix[4]tubes 15-18, respectively (Figure 16).

Figure 16. MacroModel 7.1 (Amber* Force Field) space-filling representation of nanotubular structures 15-18 (side and top views).
2.3.2. *Synthesis of Calix[4]tubes*

The synthesis of calix[4]tubes 15-18 is based on a straightforward modular strategy which incorporates reliable Williamson-type alkylation of alcohols. To immobilize the calix[4]arenes in the four conformations (cone, partial cone, 1,2-alternate, and 1,3-alternate), substituents bulkier than the ethyl group must be introduced into the four phenolic groups. The conformation in which the calix[4]arene is fixed upon derivatization depends on the reaction temperature, the solvent, the base, the *para*-substituents of the calixarene, and the reactivity of the electrophile. A general method has been developed for the preparation of tetra-O-alkylated calix[4]arenes in the 1,3-alternate conformation. 1,3-alternate calix[4]arenes can be obtained selectively either by alkylating the four phenolic groups of unsubstituted calix[4]arenes or by alkylating the two remaining phenolic groups of diametrically di-O-alkylated calix[4]arenes, using CsCO₃ as base. The Cs⁺ has been viewed to act as template metal cation in this transformation because of the high affinity of 1,3-alternate calix[4]arene derivatives with Cs⁺ ion.

Bis-calix[4]tube 15 was synthesized via coupling of diol 22 with ditosylate 23 according to Scheme 10. The first important procedure involved here is the reaction of 20 with 2-(tert-butyl(dimethyl)siloxy)ethanol-p-toluenesulfonate in the presence of CsCO₃ to yield 1,3-alternate-21. After desilylation, diol 22 was tosylated to form 23. The second important procedure is the connection of 1,3-alternate-22 and 23 in the presence of NaH to produce tube 15 in 55% yield.
The trimeric tube 16 was synthesized according to Scheme 11. The key step in the synthesis is the formation of 26 which serves as the central calixarene unit of the tube. Treatment of the parent calix[4]arene 19 with ethyl bromoacetate in the presence of Cs₂CO₃ afforded 24 in one step. Reduction of 24, followed by tosylation produced calix[4]arene 26. Finally, 26 was reacted with 2 equivalents of diol 22 in the presence of NaH to form trimeric tube 16 in 70% yield.

Tube 17, which contains four calixarenes, was prepared by reaction of biscalixarene diol 27 with derived from it ditosylate 28 in 64% yield (NaH, K₂CO₃, THF). Finally, reaction of two equivalents of diol 27 with tetratosylate 26 under the
same conditions afforded pentameric nanotube 18 in remarkable 82% yield (Scheme 12).


Syntheses of precursors for tubes 17 and 18 were based on conventional calixarene transformations (Scheme 13). Calix[4]arene 29 was obtained by alkylation of the parent calix[4]arene 19 with 2-(benzyloxy)ethanol p-toluene sulfonate and K$_2$CO$_3$ in hot MeCN in 62% yield. It was further alkylated with 2-(tert-butyldimethylsilox)ethanol- p-toluenesulfonate and Cs$_2$CO$_3$ in DMF with the formation of 1,3-alternate calix[4]arene 30. Removal of the protecting group resulted in calixarene 31. This was coupled to ditosylate 23 in THF in the presence of NaH as a base. This afforded a tubular biscalixarene 32 in 56%, which was subsequently debenzylated (H$_2$, Pd/C, AcOH, THF) to give derivative 27 in 82% yield. This was smoothly (86%) converted into ditosylate 28 by using p-toluenesulfonyl chloride, Et$_3$N and 4-(dimethylamino)-pyridine (DMAP) in CH$_2$Cl$_2$.

2.3.3 X-ray Analysis of Calix[4]tubes

Single crystals of calix[4]arene 31 suitable for x-ray analysis were obtained by slow evaporation of CH$_2$Cl$_2$-CH$_3$OH (96:4) solution. The x-ray crystal structure of the compound revealed the calix[4]arene adopted the 1,3-alternate conformation (Figure 17). The diameter of the calixarene cavity was measured to be 6 Å in diameter, which is typical for the 1,3-alternate conformation.$^{52,53}$

![Figure 17. X-ray crystal structure of calix[4]arene 31. Hydrogens are omitted for clarity.](image)

Unequivocal evidence of multiply-connected 1,3-alternate calix[4]arenes was provided by x-ray crystallographic structures of calix[4]tubes 15 and 16. Single crystals of calix[4]tubes 15 and 16 were grown by slow diffusion of CH$_3$OH in CHCl$_3$ solution at room temperature. X-ray analysis of the crystals revealed 1,3-alternate calix[4]arenes rigidly linked with diethylene glycol bridges to form hollow cylinders with diameters cavities of approximately 6 Å and lengths of 17 and 26 Å, respectively (Figure 18). The
inner tunnels are defined by two cofacial pairs of aromatic rings oriented orthogonally along the cavity axis.

Figure 18. X-ray crystal structures of calix[4]tubes 15 and 16 (side and top views; O = red, C = gray). Hydrogen atoms are omitted for clarity.

Crystal packing of nanotube 15 shows alternating rows of molecules oriented diagonally in two directions (Figure 19). The nanotubes in a row are parallel to each other and are separated by about 4 Å. They also stack together, though slightly distorted, to form a long cylindrical tunnel. The intermolecular distance between stacked nanotubes is about 12 Å. The solvent molecules occupy the vacant spaces between the tubes.
Surprisingly, a more organized packing is observed for nanotube 16. The nanotubes are packed head-to-tail in straight rows with solvent molecules occupying the vacant spaces between the tubes. The crystal packing also shows a particularly appealing supramolecular structure with the neighboring nanocylinders aligned parallel to each other (Figure 20). In each nanocylinder, molecules are twisted by 90° relative to each other, and the Ar-O-Pr propyl groups effectively occupy the voids between the
adjacent molecules. The intermolecular distance between two neighboring tubes in the nanocylinder is around 10 Å, while the calixarene units within the tube are separated from each other by about 9 Å. With this arrangement, the nanotubes stack efficiently to form long, infinite cylinders. The unique linear nanostructures maximize the intermolecular van der Waals interactions in the crystal through the overall shape simplification. This supramolecular order is not observed in shorter nanotube 15, and hence may have been influenced by the tube length.

Figure 20. Nanotube bundles. (A) Angular and (B) side views of the crystal packing of nanotube 16 into infinite nanocylinders and the parallel stacking of neighboring nanotubes. Solvent molecules and hydrogen atoms are omitted for clarity.
2.4 Conclusions

Multiple calix[4]arenes in the 1,3-alternate conformation can be covalently connected to build robust synthetic nanotubes by conventional organic protocols. The length of the nanotubes can be controlled precisely and easily. Longer tubes can effectively pack into infinite tubular bundles in the solid state. Conceptually, these nanotubes can be filled with guests by applying the unique chemistry between calix[4]arenes and nitrosonium cations (NO⁺).
CHAPTER 3
FILLING OF NANOTUBES

3.1 Encapsulation Studies

Monitoring entrapped guests inside SWNTs requires a combination of various spectroscopic and microscopic techniques. Especially important are high resolution TEM and FTIR spectroscopy as they allow the study of the location of trapped molecules and their molecular vibrations, respectively.\textsuperscript{20} While solution studies with SWNTs are still a challenge because of their poor solubility, progress with synthetic nanotubes has been slow because of poor or unstable encapsulation complexes. For example, the first calixarene-derived nanotubes, designed as channels for small metal ions, showed only weak complexation abilities, as the calixarene tunnel did not bind metal cations.\textsuperscript{57,59} However, the situation is different when calixarenes and NO\textsuperscript{+} guests are employed. As mentioned in the previous chapter, simple calix[4]arenes reversibly interact with NO\textsubscript{2}/N\textsubscript{2}O\textsubscript{4} and entrap reactive NO\textsuperscript{+} cation within their \(\pi\)-electron rich interiors. Stable nitrosonium complexes are formed upon addition of a Lewis acid (SnCl\textsubscript{4}).\textsuperscript{61}

We will show here how nanotubes \textbf{15-18} can be easily filled upon NO\textsubscript{2}/N\textsubscript{2}O\textsubscript{4} fixation, as each calixarene unit can accommodate one NO\textsuperscript{+} guest.
3.1.1. Reactions with \( \text{NO}_2/\text{N}_2\text{O}_4 \)

Addition of excess \( \text{NO}_2/\text{N}_2\text{O}_4 \) to nanotubes 15-18 in (CHCl\(_2\))\(_2\) in the presence of SnCl\(_4\) or BF\(_3\)•Et\(_2\)O resulted in the formation of nitrosonium complexes 33-36 (Scheme 14). Complexes 33-36 were characterized by UV-vis, FTIR and \(^1\)H NMR spectroscopy, which display typical features of simple calix[4]arene-\(\text{NO}^+\) species.\(^{60,61}\)

![Diagram of filling calix[4]arene nanotubes](image)

<table>
<thead>
<tr>
<th>n</th>
<th>15: n = 0</th>
<th>16: n = 1</th>
<th>17: n = 2</th>
<th>18: n = 3</th>
<th>33: n = 0</th>
<th>34: n = 1</th>
<th>35: n = 2</th>
<th>36: n = 3</th>
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</table>


The complexes exhibit a characteristic, deep purple color. Broad charge-transfer bands\(^{62,63}\) are observed at \(\lambda_{\text{max}} \sim 520\) nm in the absorption spectra of all these nanotubes (Figure 21). The charge-transfer only occurs when \(\text{NO}^+\) guests are tightly entrapped...
inside the calixarene cavities.\textsuperscript{60} Similar experiments conducted with wider and more flexible calix[5]-, calix[6]-, and calix[8]arenes did not lead to NO\textsuperscript{+} entrapment, and consequently, did not produce the characteristic color change.\textsuperscript{74}

![UV-vis absorption spectra](image)

Figure 21. UV-vis absorption spectra ((CHCl\textsubscript{2})\textsubscript{2}, 298 K) of nitrosonium complexes 33-36 (A to D).

Further evidence of the guests’ presence and location inside nanotubes 15-18 can be deduced from \textsuperscript{1}H NMR analysis (Figures 22 and 23).

All three groups of the propyl Ar-O-Pr protons in 33-36 were observed significantly downfield (\(\Delta\delta \sim 1\) ppm) compared to empty tubes 15-18. For example, the
OCH₂ protons of empty tubes 15-18 appears as a triplet at 3.3 ppm shifted to 3.9 ppm in complexes 33-36. This observation is similar to simple calixarenes where the OCH₂ protons of calixarene 13 shifted downfield from 3.54 ppm to 3.87 ppm in complex 14 (see Figure 15, page 31). This implies that there are NO⁺ cations located at both ends of the nanotubes, occupying the terminal calixarene compartments.

Figure 22. Partial ¹H NMR spectra (500 MHz, (CDCl₂)₂, 295 K) of nanotubes 15-16 and their complexes: (a) nanotube 15, (b) filled nanotube 33, (c) nanotube 16, (d) filled nanotube 34. The residual solvent signals are marked with (●).
Figure 23. Partial $^1$H NMR spectra (500 MHz, (CDCl$_2$)$_2$, 295 K) of nanotubes 17-18 and their complexes: (a) nanotube 17, (b) filled nanotube 35, (c) nanotube 18, (d) filled nanotube 36. The residual solvent signals are marked with (●).

Downfield shifts ($\Delta \delta > 1$ ppm) of the glycol Ar-O-CH$_2$ and CH$_2$-O-CH$_2$ protons situated in the middle of the tubular structures, were also observed. In empty tubes 15-18, the Ar-O-CH$_2$ protons situated at around 3.6 ppm shifted to 4.3 ppm upon complexation. For the CH$_2$-O-CH$_2$ protons, their signals at 2.6 ppm in tubes 15-18 were seen at around 4.1 ppm in complexes 33-36. These observations indicated that the middle calixarene(s) in the tubes are filled with NO$^+$ as well. It also suggests that in addition to the charge-transfer, strong cation-dipole interactions between the calixarene oxygen atoms and the entrapped NO$^+$ take place.
A surprising behavior was observed for the aromatic protons. Upon complexation, all of the aromatic protons in empty tube 15 shifted downfield except for a triplet which shifted upfield at 6.3 ppm. This behavior was also observed for longer tubes 16-18, but with increasing sets of triplets found at 6.4-6.7 ppm in complexes 34-36. This signal was assigned to the para-aromatic CH protons positioned in the middle of the tube (highlighted in red in Figure 22, right), based on the COSY and NOESY spectrum of complex 33. This assignment was confirmed by NOESY spectrum for the nitrosonium-filled nonsymmetrical O,O'-dimethylated derivative of 27 (designated as 27b). As expected for the nonsymmetrical dimeric tube 27b, two sets of triplets (1:1) were observed at 6.3 and 6.2 ppm upon complexation of NO⁺. The triplet at 6.3 ppm belongs to the set of proton signals similar to the dimeric tube-NO⁺ complex 33. A possible explanation for the upfield shift of the aromatic para-protons is presented in Section 3.1.3 (page 53).

3.1.2. Stoichiometry of Nitrosonium Complexes

Using NO₂/N₂O₄ gases, we have demonstrated the ability of nanotubes 15-18 to encapsulate multiple NO⁺ guests. However, we encountered some difficulties in handling small and precise quantities of NO₂/N₂O₄. Moreover, NO₂/N₂O₄ is so aggressive that it reacts with nanotubes upon standing by nitrosating/nitrating the aromatic rings. This has also been observed with simple calixarenes. These aspects complicate the determination of the stoichiometry.

Molecular modeling and analogies with simpler calixarene-NO⁺ complexes suggest that one calixarene fragment in the nanotubes can accommodate only one NO⁺
guest. Therefore, nanotubes 33-36 should have two, three, four and five NO\textsuperscript{+} species, respectively. Higher stoichiometries of NO\textsuperscript{+} were ruled out because there is simply no room to accept larger number of repulsive cations.

Recently, we found alkyl nitrites (AlkO-N=O) to be more reliable sources of NO\textsuperscript{+} for determining stoichiometry of the complexes.\textsuperscript{75} Alkyl nitrites are known to be effective NO donors in medicine, and act as nitrosating reagents.\textsuperscript{76,77} Alkyl nitrites are much easier to handle than NO\textsubscript{2}/N\textsubscript{2}O\textsubscript{4} gases. They are stable, nonvolatile liquids. They are easy to transfer by conventional laboratory pipettes. Thus, we can precisely determine the concentration of NO\textsuperscript{+} being reacted with the nanotubes, and the stoichiometry of the complexes by titration.

Addition of one equivalent \textit{t}-butyl nitrite to the CDCl\textsubscript{3} solution of calix[4]arene 37 in the presence of 4 equivalents of SnCl\textsubscript{4} resulted in a rapid formation of a deep purple solution. The UV-vis spectrum showed a broad charge-transfer band at $\lambda_{\text{max}} \sim$580 nm, which is characteristic for arene-NO\textsuperscript{+} complexes.\textsuperscript{61,78}

\textsuperscript{1}H NMR spectrum of the complex also revealed similar features with simple calix[4]arenes-NO\textsuperscript{+} complexes.\textsuperscript{60,61} The spectrum revealed new sets of calixarene signals which are clearly distinguished from free calixarene 37 (Figure 24). The aromatic protons of free 37 were recorded as a singlet at 7.00 ppm. In the nitrosonium complex 38, it was transformed into a singlet at 7.02 ppm. The methylene bridge CH\textsubscript{2} protons of 37 were seen as a singlet at 3.74 ppm, while in complex 38, this was observed at 3.61 ppm. The OCH\textsubscript{2} protons in 37 were recorded at 3.39 ppm, and they shifted to 3.77 ppm in complex 38.
Figure 24. Portions of the $^1$H NMR spectra (500 MHz, CDCl$_3$, 295 K) of (A) calixarene 37 and 4 equiv of SnCl$_4$, (B) calix[4]arene-NO$^+$ complex 38. Residual CDCl$_3$ signals are marked with “•”. 75

We observed that the NO$^+$ transfer only occurs in the presence of SnCl$_4$. The Lewis acid most probably interacts with the nitrite C-O-N oxygen atom and facilitates the cleavage of the O-N bond (Figure 24, top). 79 It may also stabilize the complexes by coordinating to the counter ion, similar to known arene-nitrosonium nitrate complexes. 80

Addition of $t$-butyl nitrite to nanotubes 15-18 in (CDCl$_2$)$_2$ in the presence of excess SnCl$_4$ or tetrafluoroacetic acid (TFA) also led to the rapid formation of the corresponding calixarene-NO$^+$ complexes. These were identified by NMR, FTIR and
UV-vis spectroscopy, and show similar features with the previously described complexes formed using NO$_2$/N$_2$O$_4$ (See Section 3.1.1, pages 43-47).

Figure 25. Titration of nanotube 15 with t-butyl nitrite. Portions of the $^1$H NMR (500 MHz, (CDCl)$_2$, 295 K) of (A) empty tube 15, (B) 15 + 4 equiv SnCl$_4$, (C) addition of 1 equiv tBuONO, (D) addition of 2 equiv tBuONO, (E) 33 prepared from NO$_2$/N$_2$O$_4$.

Upon stepwise addition of t-butyl nitrite, the $^1$H NMR signals of empty tubes 15-18 and complexes 33-36 can be seen separately and in slow exchange. This is typical for host-guest complexes with high exchange $\Delta G^\ddagger$ barriers (>15 kcal/mol) and/or high
association constants ($K_{\text{assoc}} > 10^6 \text{ M}^{-1}$).\textsuperscript{63,81} Titration experiments also show that two equivalents of t-butyl nitrite were needed to fill dimeric tube 15 (Figure 25), and adding three equivalents of the nitrite completely filled trimeric nanotube 16 (Figure 26).

Figure 26. Titration of nanotube 16 with t-butyl nitrite. Portions of the $^1$H NMR (500 MHz, (CDCl)$_2$, 295 K) of (A) empty tube 16, (B) 16 + 6 equiv SnCl$_4$, (C) addition of 1 equiv tBuONO, (D) addition of 2 equiv tBuONO, (E) addition of 3 equiv tBuONO, (F) 34 prepared from NO$_2$/N$_2$O$_4$.

Analogously, a 1:4 tube-NO$^+$ ratio was established for longer tube 17, possessing four calixarene units (Figure 27). Further addition of the nitrite did not
change the NMR spectra. This confirms the stoichiometry of the nanotube complexes, which possess one NO$^+$ per calixarene unit. A similar trend is expected for tube 18, although the titrations in this case are less accurate due to the broadening of signals and low solubility of the complex.

![NMR Spectra](image)

**Figure 27.** Titration of nanotube 17 with $t$-butyl nitrite. Portions of the $^1$H NMR (500 MHz, (CDCl$_2$)$_2$, 295 K) of (A) empty tube 17, (B) 17 + 8 equiv SnCl$_4$, (C) addition of 1 equiv tBuONO, (D) addition of 2 equiv tBuONO, (E) addition of 3 equiv tBuONO (F) addition of 4 equiv tBuONO, (G) 35 prepared from NO$_2$/N$_2$O$_4$. 

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3.1.3. *FTIR* Analysis

Based on molecular modeling, the NO$^+$ filled nanotubes 33-36 adopt a somewhat shrunken structure, with all *gauche* conformations about the glycol C-C bonds. On the other hand, empty tubes 15-18 possess all *anti* C-C conformation, which was also evident from the X-ray structures of tubes 15 and 16 (see Fig.18, p. 38). The experimental proof came from FTIR studies in (CHCl$_2$)$_2$. In empty tubes 15-18 the band corresponding to the *anti* C-C conformation at $\nu = 1340$ cm$^{-1}$ was observed. In complexes 33-36 this band disappeared and a new band at $\nu = 1355$ cm$^{-1}$ appeared, which is characteristic for the gauche C-C conformer (Figure 28). In the literature, these absorptions are attributed to the CH$_2$ wagging.$^{82,83}$

![Figure 28](image)

Figure 28. Portions of the IR spectra ((CDCl$_2$)$_2$, 295 K) of (A) nanotube 15, (B) filled tube 33, and (C) t-butyl nitrite. The band corresponding to the *anti* and *gauche* C-C conformations are marked. The band at $\nu = 1370$ cm$^{-1}$ belongs to t-butyl nitrite.
One reasonable explanation for such conformational change might be a participation of the basic glycol CH\textsubscript{2}OCH\textsubscript{2} oxygens in NO\textsuperscript{+} complexation. To bring in close proximity and thus contribute to dipole-cation interactions with the entrapped NO\textsuperscript{+}, the glycol chains should adopt the more compact gauche C-C conformation (Figure 29). As a result, the filled nanotubes are shorter. The shrinking also brings the aromatic rings from the neighboring calixarene units closer to each other. Thus, the para-aromatic CH protons of tubes 33-36 that face each other appear shielded and are seen upfield at 6.2 – 6.4 ppm in the \textsuperscript{1}H NMR spectra. These signals can be used as a characteristic signature for the complex formation.

![Figure 29. Conformational transition about the glycol C-C bonds.](image)

Vibrational spectra also allowed us to obtain unique information on the bonding of multiple NO\textsuperscript{+} species inside tubes 15-18 in solution. From the literature, the nitrosonium salts NO\textsuperscript{+}Y\textsuperscript{-} (Y\textsuperscript{-} = BF\textsubscript{4}$^-$, PF\textsubscript{6}$^-$, AsF\textsubscript{6}$^-$) exhibit a single stretching band at
\(\nu(\text{NO}^+) = 2270 \text{ cm}^{-1}\) in \(\text{CH}_3\text{NO}_2\) solutions,\(^{84}\) and the stretching frequency of the neutral diatomic NO gas is \(\nu(\text{NO}) = 1876 \text{ cm}^{-1}.\(^{84,85}\)

![Figure 30. Portions of the IR spectra (\((\text{CDCl}_2)_2\), 295 K) of calix[4]arene-NO\(^+\) complex 14 and completely filled nanotubes 33-36.](image)

In calixarene-NO\(^+\) complex 14, the NO\(^+\) band significantly shifted (\(\Delta\nu = 312 \text{ cm}^{-1}\)) to lower energies compared to free NO\(^+\) cation, and appeared at \(\nu(\text{NO}^+) = 1958 \text{ cm}^{-1}\) in (CHCl\(_2\))\(_2\) (Figure 30). This is due to strong electron donor-acceptor interactions between the encapsulated NO\(^+\) and \(\pi\)-electron rich aromatic walls of the calixarene.\(^{64,78}\) Dimeric complex 33 also exhibited similar shifts for the NO\(^+\) guests at \(\nu(\text{NO}^+) = 1958 \text{ cm}^{-1}\). Interestingly, for longer tubes 34-36 two absorption bands at \(\nu(\text{NO}^+) = 1958 \text{ cm}^{-1}\) and 1940 \text{ cm}^{-1}\) were observed in (CHCl\(_2\))\(_2\). For trimeric tube 34, these two bands have comparable intensities, while in longer tubes 35 and 36 the band at \(\nu(\text{NO}^+) = 1940 \text{ cm}^{-1}\)
dominates. This band was assigned to the NO$^+$ guest(s) which are situated in the middle of the tubes. Apparently, they are somewhat more strongly bound to the nanotubes walls. One possible explanation might be the participation of the glycol CH$_2$OCH$_2$ oxygens (Figure 29). As discussed earlier for the anti-gauche conformational transition upon complexation, these oxygens appear in close proximity and thus contribute to dipole-cation interactions with the entrapped NO$^+$. Accordingly, FTIR spectroscopy can be used to monitor multiple entrapped NO$^+$ guests inside nanotubes tubes 33-36 and even distinguish among them.

3.2 Conclusions

Nanotubes 15-18 can be filled with multiple NO$^+$ guests, producing deep colored solutions. They exhibit typical calix[4]arene-NO$^+$ complexes as evidenced by UV-vis, $^1$H NMR and FTIR spectroscopy. The stoichiometry of the complexes reveals the encapsulation of one NO$^+$ guest per calixarene cavity. The filling process is cooperative and causes conformational changes within the nanotubes. NO$^+$ guests entrapped deep inside the nanotube experience stronger electron donor-acceptor interactions compared to guests near the ends of the nanotube.
CHAPTER 4
HOST-GUEST DYNAMICS OF FILLED NANOTUBES

4.1 Introduction

Aside from synthetic nanotubes, there are a number of designs and syntheses of nanoscale molecular containers that has emerged over the last decade. These include cavitands, carcerands, hemicarcerands, and capsules (Figure 31). Cavitands are synthetic host molecules with open-ended cavities large enough to bind complementary organic molecules and ions. The concave inner surfaces of cavitands can be modified to have various shapes, with either integrated or appended binding sites. Carcerands are closed-surface structures but with enforced inner cavities large enough to incarcerate smaller organic molecules. The portals of carcerands are too narrow to allow the guest to escape without breaking covalent bonds. Thus, carcerands hold guests permanently. Hemicarcerands, on the other hand, have larger portals which allow the entrapped guest to escape at high temperature. Self-assembling capsules are receptors with enclosed cavities formed through reversible noncovalent interactions between two or more subunits. They can trap guests but may release them without breaking covalent bonds and under milder conditions.

Synthetic nanotubes, on the hand, possess a different topology, are open from both ends, and therefore, may feature different guest dynamics upon encapsulation.
Synthetic nanotubes can also be filled with multiple guests in a one-dimensional morphology inside its hollow structure, unlike cavitands, carcerands, hemicarcerands and capsules.

Figure 31. Nanoscale molecular containers: (A) cavitand, (B) carcerand, (C) hemicarcerand, (D) capsule, (E) nanotube.86

4.2 Guest Exchange and Dynamics

It is evident from $^1$H NMR studies that the NO$^+$ exchange in and out of the nanotubes 15-18 is slow on the NMR time scale. Upon stepwise addition of $t$-butyl nitrite, the $^1$H NMR signals of empty tubes 15-18 and complexes 33-36 can be seen separately. Moreover, the NO$^+$ complexation does not influence the symmetry of nanotubes 15-18 at 295 K. The number of the propyl OCH$_2$, the glycol CH$_2$OCH$_2$ and ArOCH$_2$, and the aromatic proton signals for 33-36 does not change. This implies that the NO$^+$ guests, with the van der Waals dimensions of $\sim$2 Å, freely rotate along the N-O
axis and also tumble within the cavity at room temperature. Similar dynamics were also noticed for simple calixarene-NO\textsuperscript{+} complexes.\textsuperscript{61}

We also found that complexes 33-36 form even when less than stoichiometric amounts of \textit{t}-butyl nitrite are added. From the integration, it was possible to quantitatively estimate the concentration of complexes 33 and 34. For example, addition of 1 equivalent of \textit{t}-butyl nitrite to dimeric tube 15 produces 50±5\% of fully occupied complex 33, and addition of 2 equivalents of \textit{t}-butyl nitrite to trimeric tube 16 produces 55±5\% of fully occupied complex 34, which is much higher than simple statistical distribution, when partially filled tubes are considered. This may suggest that the strong binding allowed each calixarene unit in the tube to complex NO\textsuperscript{+} independently from the others. This behavior may also reflect a cooperative effect\textsuperscript{87} on nitrosonium binding with the tube, in which the binding of one NO\textsuperscript{+} enhances the affinity of the tube towards another NO\textsuperscript{+} guest. As discussed in the previous chapter, the encapsulation of NO\textsuperscript{+} guests leads to conformational changes about the glycol bridges (see Fig. 29, p. 54). This conformational change may bring the glycol oxygen lone pairs in close proximity with adjacent oxygen lone pairs. The lone pair-lone pair repulsion can contribute to the thermodynamic instability\textsuperscript{88} of the incompletely filled nanotube. This enthalpic gain, however, is compensated by further binding of NO\textsuperscript{+} guests, resulting in positive cooperativity. This may be the reason behind the observed high formation of fully occupied complexes in the titration experiments.

Cooperativity is well known to take place in biological systems, for example in the oxygenation of hemoglobin.\textsuperscript{89} This tetrameric protein binds four individual oxygen
molecules with increasing affinity until all four binding sites are occupied in a positive cooperative manner. The observed cooperativity is attributed to conformational changes in the quaternary structure of the protein, although a structural explanation for the low affinity quaternary state (unbounded protein) remains debatable.

Figure 32. Cooperative reversible encapsulation of two pyrazine guests (G) in bis-capsules. (A) Schematic representation of a carceplex. (B) Formation of bis-capsules by encapsulation of guests.90

Cooperativity is also observed by Sherman in a biscarceplex, where two carceplexes are covalently linked such that one guest molecule is entrapped in each of the two adjacent but physically separate chambers.90 The biscarceplex encapsulates one pyrazine molecule in each chamber. The binding of one guest causes two adjacent bowls to clamp down and form a filled capsule (Figure 32). This also forces the remaining two bowls to clamp down as well, forming an empty cavity which is thermodynamically unstable. Thus, a 1:1 ratio of host to guest is not formed in significant quantities at equilibrium.
The filled nanotubes 33-36 are stable in dry solution at room temperature within 24 hours, but can readily dissociate upon addition of H₂O, producing empty nanotubes 15-18. The process however is not reversible. The released NO⁺ species are converted to nitrous acid and complexes 33-36 cannot be regenerated.

We found that 18-crown-6 can reversibly remove the encapsulated NO⁺ species. It is known that crown ethers form stable complexes with NO⁺.⁹¹-⁹³ For example, the reaction of 18-crown-6 with NOBF₄ afforded a 1:1 complex. In the ¹H NMR spectrum, the OCH₂CH₂O protons, seen as a singlet at 3.67 ppm for 18-crown-6 is shifted downfield to 3.7 ppm for the complex. It also indicates a rapid exchange in the NMR time scale between the free crown molecule and the complex. From the IR spectrum, new absorption bands for the N-O stretching frequency at ν = 2250 cm⁻¹ appeared in CH₂Cl₂.⁹⁴ The complexation constant was estimated at K > 10⁴ M⁻¹ based on the oxidation and reduction potentials of the complex in MeCN.⁹³

When 4 equiv of 18-crown-6 was added to the CDCl₃ solution of complex 14, free calixarene 13 was obtained. The deep purple colored solution disappeared, and the ¹H NMR spectrum changed (Figure 33). The aromatic proton signals for the nitrosonium complex 14 seen as a triplet and a doublet at 7.2 and 7.1 ppm were transformed into a doublet and a triplet at 6.9 and 6.7 ppm, which corresponds to free calixarene 13. Likewise, the methylene bridge CH₂ and OCH₂ protons of 14 seen as a triplet and a singlet at 3.9 and 3.6 ppm were transformed into a singlet and a triplet at 3.6 and 3.5 ppm. Addition of excess SnCl₄ regenerated the complex, forming the deep purple colored solution, and restored the ¹H NMR signals corresponding to complex 14.
Figure 33. Nitrosonium exchange with simple calix[4]arene 13. Selected portions of $^1$H NMR (500 MHz, CDCl$_3$, 295 K) of: (A) nitrosonium complex 14, (B) addition of 4 equiv 18-crown-6, (C) same as B with 4 equiv SnCl$_4$.

When 2 equiv of 18-crown-6 was added to (CDCl$_2$)$_2$ solutions of complex 33, empty nanotube 15 was regenerated, and the deep purple color disappeared. The process can be followed by $^1$H NMR spectroscopy (Figure 34). The NO$^+$ transfer process is slow in the NMR time scale as shown by the presence of both complex 33 and empty tube 15.

Surprisingly, addition of 4 equiv of SnCl$_4$ to the same solution fully restores complex 33. There have been reports in the literature showing that SnCl$_4$ form complexes with crown ethers.$^{95-97}$ X-ray analysis on a single crystal of SnCl$_4$ complexed to 18-crown-6 shows two adjacent oxygen atoms of the crown ether coordinated to Sn (IV).$^{97}$ In our hands, the addition of 4 equiv of SnCl$_4$ to a (CDCl$_2$)$_2$ solution containing
only 18-crown-6 resulted in the shift of the OCH\textsubscript{2}CH\textsubscript{2}O proton signal of 18-crown-6 seen as a singlet from 3.6 ppm to 3.7 ppm. This indicates an interaction between SnCl\textsubscript{4} and 18-crown-6 in solution. In the system under investigation, the OCH\textsubscript{2}CH\textsubscript{2}O proton signal of 18-crown-6 is also observed as a singlet at 3.7 ppm upon addition of SnCl\textsubscript{4}. This indicates the SnCl\textsubscript{4} complexation and its competitive role in replacing NO\textsuperscript{+} from the 18-crown-6-NO\textsuperscript{+} complex (Figure 35). This observation is important, since in this case, foreign species can be replaced and returned back without decomposition or changing the solution polarity.

Figure 34. Nitrosonium exchange with nanotube 15. Selected portions of the $^1$H NMR spectra (500 MHz, (CDCl\textsubscript{2})\textsubscript{2}, 295 K), of: A. nanotube 15. B. filled nanotube 33. C. same as B with 1 equiv of 18-crown-6. D. same as B with 2 equiv of 18-crown-6. E. same as D with 2 equiv of SnCl\textsubscript{4}. F. same as D with 4 equiv of SnCl\textsubscript{4}. 63
Nitrosonium transfer can also be demonstrated with complex 34. In this case, 3 equiv of 18-crown-6 are required to completely remove NO\(^+\) species and regenerate nanotube 16. Stepwise addition of 18-crown-6 slowly bleaches the deep purple solution of the complex 34. Again, this process can be monitored by \(^1\)H NMR (Figure 36). The transformation of complex 34 to empty tube 16 and vice versa is slow in the NMR time scale, as both 16 and 34 species are observed in the spectra. Addition of 6 equiv of SnCl\(_4\) is enough to bring back the NO\(^+\) guests into the nanotube.
Figure 36. Nitrosonium exchange with nanotube 16. Selected portions of the $^1$H NMR spectra (500 MHz, (CDCl$_2$)$_2$, 295 K), of: A. nanotube 16. B. filled nanotube 34. C. same as B with 1.5 equiv of 18-crown-6. D. same as B with 3 equiv of 18-crown-6. E. same as D with 3 equiv of SnCl$_4$. F. same as D with 6 equiv of SnCl$_4$.

The NO$^+$ transfer between calixarene nanotube 16 and 18-crown-6 can also be observed by IR spectroscopy. Complex 34 shows two absorption bands at $\nu$(NO$^+$) = 1955 cm$^{-1}$ and 1940 cm$^{-1}$. Upon addition of 18-crown-6, these two bands diminished and a new absorption band at $\nu$(NO$^+$) = 2248 cm$^{-1}$ appeared (Figure 37). This new band
corresponds to the NO⁺ encapsulated in 18-crown-6. With the addition of excess SnCl₄ to the same solution, the two absorption bands at 1955 cm⁻¹ and 1940 cm⁻¹ reappears, and the band at 2248 cm⁻¹ disappears.

Figure 37. Selected portions of the IR spectra ((CHCl₂)₂, 295 K) of (A) complex 34, (B) complex 34 + 3 equiv 18-crown-6, and (C) same as B + 6 equiv SnCl₄. Arrows indicate increase (arrow down) and decrease (arrow up) of bands.

Based on modeling, NO⁺ species can enter and leave the nanotube either through its open ends (Route A, Figure 38) or the middle gates between the calixarene modules (Route B, Figure 38). The approach and exit through the ends of the tube is less hindered, and thus more favored. Besides, the middle gates between the calixarene units
become narrower due to the glycol conformational changes from *anti* to *gauche* upon complexation (see Figure 29). The encapsulated NO⁺ species should also avoid electrostatic repulsions with each other. Most probably, the tube filling and release occurs through the guest tunneling along the interior.

Figure 38. Potential routes for nanotube filling and release of NO⁺ guests.
4.3 Conclusion and Outlook

Unlike other developed nanoscale molecular containers, synthetic nanotubes can be filled with multiple guests in one-dimensional morphology which leads to unique host-guest dynamics such as cooperativity. In the case of calix[4]arene-based nanotubes, NO$^+$ serves as the filling material. The tunnel of the nanotube allows the NO$^+$ guests to freely rotate along the N-O axis and also tumble within the cavity at room temperature. Though the filled nanotube is stable, it allows the release and re-entry of guests within its hollow structure. NO$^+$ can be transferred to and from another host such as 18-crown-6. The guest exchange and dynamics can be monitored by conventional spectroscopic techniques.

Potential applications of synthetic nanotubes such as nanowires, sensors, and molecular storage containers of reactive species can be explored. Generation of gas molecules inside the nanotubes such as NO can also be studied. Similar designs can be developed to fill synthetic nanotubes with other species.
CHAPTER 5

EXPERIMENTAL SECTION

5.1 General Information

All reagents and solvents were purchased from commercial suppliers (Aldrich, Acros Chemicals, Cambridge Isotope Laboratories, etc.) and were used without purification unless otherwise specified. Melting points were determined on a Mel-Temp apparatus (Laboratory Devices, Inc.) and are uncorrected. $^1$H, $^{13}$C NMR, COSY and NOESY spectra were recorded at 22 ± 1 °C on JEOL 300 and 500 MHz spectrometers. Chemical shifts were measured relative to residual non-deuterated solvent resonances. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer using KBr pressed pellet for solids or solution between NaCl plates and reported in cm$^{-1}$. UV-vis spectra were measured on a Varian Cary-50 spectrophotometer. Mass spectra were recorded at the Scripps Center for Mass Spectrometry (La Jolla, CA). High Resolution MALDI FT mass spectra were obtained on an IonSpec Ultima FTMS. ESI-TOF mass spectra were obtained on an Agilent ESI-TOF mass spectrometer. MALDI TOF mass spectra were obtained on an Applied Biosytems Voyager STR (2). Elemental analysis was performed on a Perkin-Elmer 2400 CHN analyzer. For column chromatography, Silica Gel 60 Å (Sorbent Technologies, Inc.; 200–425 mesh) was used. All experiments with moisture- and/or air-sensitive compounds were run under a dried nitrogen
atmosphere. Parent tetrahydroxycalix[4]arene 19, and calix[4]arene derivatives 20 and 24 were prepared according to the published procedures. NO₂/N₂O₄ was generated from copper and concentrated HNO₃. Molecular modeling was performed using commercial MacroModel 7.1 with Amber* Force Field.

5.2 Experimental Procedures and Data

25,27-Bis(1-propyloxy)-26,28-bis(2-(tert-butyldimethylsiloxy)ethyloxy)calix[4]-arene, 1,3- alternate (21): A suspension of 25,27-dihydroxy-26,28-bis(1-propyloxy)calix[4]arene 20 (3.0 g, 6.0 mmol), 2-(tert-butyldimethylsiloxy)ethanol p-toluenesulfonate (3.9 g, 12.0 mmol), and Cs₂CO₃ (5.7 g, 18.0 mmol) in MeCN (100 mL) was refluxed for 24 h. The solvent was removed, and the reaction mixture was treated with 10% aq acetic acid (50 mL) and CH₂Cl₂ (50 mL). The organic layer was separated, washed with 10% aq NaHCO₃ (15 mL), brine (2 x 15 mL) and dried over MgSO₄. Evaporation of CH₂Cl₂ gave a light yellow solid, which was recrystallized from MeOH to give a white solid. Yield 2.7 g (55%); mp 140-142°C; ¹H NMR (CDCl₃): δ 7.08 (d, J = 7.7 Hz, 4 H), 6.99 (d, J = 7.3 Hz, 4 H), 6.65, 6.62 (2 x t, J = 7.7, 7.3 Hz, 4 H), 3.84 (t, J = 5.5 Hz, 4 H), 3.76 (t, J = 5.5 Hz, 4 H), 3.61 (t, J = 7.0 Hz, 4H), 3.60 (2 x d, J = 13.2 Hz, 8 H), 1.81 (m, 4 H), 1.02 (t, J = 7.3 Hz, 6 H), 0.96 (s, 18 H), 0.16 (s, 12 H); ¹³C NMR (CDCl₃): δ 156.2, 155.9, 133.8, 133.5, 129.9, 129.7, 121.7, 121.5, 74.4, 73.6, 70.8, 62.5, 35.3, 26.1, 23.9, 18.5, 10.7, -5.1; FTIR (CHCl₃): ν 3069, 3030, 2932, 2859, 1453, 1250, 1198, 1093, 1044, 1008 cm⁻¹; Anal. calcd for C₅₀H₇₂O₆Si₂: C, 72.77; H, 8.79. Found: C, 72.70; H, 8.72.
**25,27-Bis(2-hydroxyethyloxy)-26,28-bis(1-propyloxy)calix[4]arene, 1,3-alternate (22):** Acetyl chloride (0.20 mL, 2.9 mmol) was added dropwise to an ice-cold mixture of CH₂Cl₂/MeOH (10 mL, 9/1, v/v), and after 30 min a solution of calix[4]arene 21 (0.3 g, 4.1 mmol) in CH₂Cl₂ (5 mL) was added. After the starting material was consumed (TLC, Hex/AcOEt, 7/3, ~1h), the reaction mixture was washed with 10% aq NaHCO₃ (5 mL), brine (5 mL) and dried over MgSO₄, and evaporated in vacuo. The residue was treated with MeOH to give derivative 22 as a colorless solid. Yield 0.23 g (95%); mp = 262-264°C; ¹H NMR (CDCl₃): δ 7.07 (d, J = 7.5 Hz, 4H), 7.04 (d, J = 7.5 Hz, 4H), 6.89 (t, J = 7.0 Hz, 2H), 6.86 (t, J = 7.0 Hz, 2H), 3.91 (AB q, J = 16.5 Hz, 8H), 3.62 (m, 4H), 3.35 (t, J = 7.0, 4H), 3.28 (m, 4H) 2.33 (t, 2H), 1.01 (m, 4H), 0.63 (t, J = 7.2 Hz, 6H); FTIR (KBr): ν 3527, 3315, 3063, 3019, 2958, 2904, 2873, 1459, 1248, 1212, 1091, 1029 cm⁻¹. The spectral and analytical data are in agreement with previously published compound which was obtained from calix[4]arene 23.⁶⁸

**25,27-Bis(2-p-toluenesulfonyloxyethyloxy)-26,28-bis(1-propyloxy)calix[4]arene, 1,3-alternate (23):** In a modified procedure, 25,27-Bis(2-hydroxyethyloxy)-26,28-bis(1-propyloxy)calix[4]arene 22 (0.65 g, 1.09 mmol), DMAP (0.025 g, 0.21 mmol), and p-toluenesulfonyl chloride (0.83 g, 4.35 mmol) were dissolved in CH₂Cl₂ (15 mL) and cooled at -5°C. Triethylamine (1.0 mL) was added, and the solution was stirred overnight at rt. The solution was evaporated to dryness, redissolved in CH₂Cl₂, then washed with 5% HCl, water, and brine. The organic layer was dried with Na₂SO₄ and evaporated to dryness. Treatment with MeOH produced...
compound 23 as colorless solid. Yield 0.84 g (86%); mp 128-130°C; \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.83 (d, \(J = 7.3\) Hz, 4H), 7.40 (d, \(J = 7.3\) Hz, 4H), 6.98 (d, \(J = 7.3\) Hz, 4H), 6.89 (d, \(J = 7.3\) Hz, 4H), 6.74 (t, \(J = 7.3\) Hz, 2H), 6.54 (t, \(J = 7.3\) Hz, 2H), 3.74 (t, \(J = 5.5\) Hz, 4H), 3.70 (AB q, \(J = 15.4\) Hz, 8H), 3.50 (t, \(J = 5.5\) Hz, 4H), 3.43 (t, \(J = 5.5\) Hz, 4H), 2.47 (s, 6H), 1.40 (m, 4H), 0.76 (t, \(J = 5.5\) Hz, 6H); FTIR (KBr): \(\nu\) 3063, 3017, 2960, 2932, 2876, 1457, 1360, 1248, 1210, 1095, 1011 cm\(^{-1}\). The spectral and analytical data are in agreement with previously published data.\(^{69}\)

25, 26, 27, 28-Tetrakis(2-hydroxyethoxy)calix[4]arene, \(1,3\)-alternate (25):
Yield 0.60 g (77%); mp > 250°C (decomp.); \(^1\)H NMR (CDCl\(_3\)): 7.11 (d, \(J = 7.7\) Hz, 8H), 6.97 (t, \(J = 7.7\) Hz, 4H), 3.97 (s, 8 H), 3.59 (t, \(J = 5.0\) Hz, 8 H), 3.21 (t, \(J = 5.0\) Hz, 8 H), 2.13 (s, 4 H); \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 156.3, 133.6, 129.8, 123.9, 71.6, 61.1, 38.3. The spectral and analytical data are in agreement with previously published data.\(^{71}\)

25,26,27,28-tetrakis(2-p-toluenesulfoxyethoxy)-calix[4]arene, \(1,3\)-alternate (26): In a modified procedure, 25, 26, 27, 28-Tetrakis(2-hydroxyethoxy)calix[4]arene 25 (0.10 g, 0.17 mmol), DMAP (8.5 mg, 0.070 mmol), and \(p\)-toluenesulfonyl chloride (0.27 g, 1.4 mmol) were dissolved in CH\(_2\)Cl\(_2\) (15 mL) and cooled at -5°C. Triethylamine (1.0 mL) was added, and the solution was stirred overnight at rt. The solution was evaporated to dryness, redissolved in CH\(_2\)Cl\(_2\), then washed with 5% HCl, water, and brine. The organic layer was dried with Na\(_2\)SO\(_4\) and evaporated to dryness. Treatment with MeOH produced compound 26 as colorless solid. Yield 0.12 g (57%);
25,27-Bis(2-benzyloxy)ethyloxy)-26,28-dihydroxycalix[4]arene (29): A suspension of parent calix[4]arene (1.0 g, 2.4 mmol), 2-(benzyloxy)ethanol p-toluene sulfonate (1.51 g, 4.9 mmol) and K$_2$CO$_3$ (0.67 g, 4.8 mmol) in MeCN (20 mL) was refluxed for 24 h. After cooling to rt, the solvent was removed under reduced pressure, and the residue was treated with 10% aq HCl (20 mL) and CH$_2$Cl$_2$ (40 mL). The organic layer was separated and washed with 10% aq NaHCO$_3$ (2 x 15 mL) and brine. The organic solution was dried over MgSO$_4$, filtered and evaporated in vacuo. The resulting pale yellow oil was solidified with MeOH (3 x 15 mL) to give product 29 as a white powder. Yield 1.03 g (62%); mp 138-140°C; $^1$H NMR (CDCl$_3$): δ 7.87 (s, 2 H), 7.33 (m, 10 H), 7.06, 6.89 (2 x d, $J = 7.5$ Hz, 8 H), 6.72, 6.65 (2 x t, $J = 7.5$ Hz, 4 H), 4.65 (s, 4 H), 4.45, 3.37 (2 x d, $J = 12.8$ Hz, 8 H), 4.18 (t, $J = 5.1$ Hz, 4 H), 3.92 (t, $J = 5.1$ Hz, 4 H); $^{13}$C NMR (CDCl$_3$): δ 153.4, 152.0, 138.2, 133.4, 129.0, 128.6, 128.5, 128.2, 128.0, 127.7, 125.4, 118.9, 75.7, 73.7, 69.2, 31.4; FTIR (KBr): ν 3333, 3062, 3028, 2928, 2861, 1467, 1453, 1355, 1250, 1200, 1123, 1090, 1045 cm$^{-1}$; Anal. calcd for C$_{46}$H$_{46}$O$_6$: C, 79.51; H, 6.67. Found: C, 79.23; H, 6.41.
25,27-Bis(2-benzyloxy)ethyloxy)-26,28-bis(2-(tert-butyldimethylsiloxy)ethyloxy)calix[4]arene, 1,3- alternate (30): A suspension of 1,3-bis(2-benzyloxy)ethyloxy) calix[4]arene 29 (1.15 g, 1.65 mmol) and Cs$_2$CO$_3$ (2.7 g, 8.3 mmol) in DMF (50 mL) was heated at 90 °C for 1 h, then a solution of 2-(tert-butyldimethylsiloxy)ethanol p-toluenesulfonate (2.74 g, 8.29 mmol) in DMF (10 mL) was added. The reaction mixture was stirred at 90 °C for 24 h. DMF was completely removed in vacuo, and the reaction mixture was treated with 10% aq acetic acid (50 mL) and CH$_2$Cl$_2$ (50 mL). The organic layer was separated, washed with 10% aq NaHCO$_3$ (15 mL), brine (2 x 15 mL) and dried over MgSO$_4$. Evaporation of CH$_2$Cl$_2$ gave a light yellow solid, which was refluxed with KI (1 g) and Et$_3$N (1 mL) in MeCN (30 mL) for 1 h. The solvent was evaporated in vacuo, and the residue was solidified with MeOH (3 x 15 mL). The resulting brownish-yellow solid was then refluxed with MeOH (25 mL) and filtered hot, washed with MeOH (3 x 15 mL), giving product 30 as a white powder. Yield 1.12 g (67%); mp 116-120 °C; $^1$H NMR (CDCl$_3$): δ 7.36 (m, 10 H), 7.07, 7.04 (2 x d, $J = 7.3$ Hz, 8 H), 6.62, 6.56 (2 x t, $J = 7.3$ Hz, 4 H), 4.66 (s, 4 H), 3.87 (m, 8 H), 3.77, 3.71 (2 x m, 8 H), 3.55 (s, 8 H), 0.96 (s, 18 H), 0.15 (s, 12 H); $^{13}$C NMR (CDCl$_3$): δ 155.8, 155.6, 138.4, 133.6, 130.0, 129.8, 128.5, 127.8, 121.9, 74.0, 73.4, 71.6, 69.7, 62.7, 34.9, 26.2, 18.5, -5.1; FTIR (CHCl$_3$): ν 3068, 3032, 2931, 2714, 1452, 1361, 1250, 1198, 1098, 1029 cm$^{-1}$; Anal. calcd for C$_{62}$H$_{80}$O$_8$Si$_2$: C, 73.77; H, 7.99. Found: C, 73.52; H, 7.93.
25,27-Bis(2-benzyloxy)ethylx)oxy)-26,28-bis(2-(hydroxy)ethylx)oxy)calix[4]arene, 1,3-alternate (31): Acetyl chloride (0.46 mL, 6.5 mmol) was added dropwise to the ice-cold mixture of CH₂Cl₂/MeOH (10 mL, 9/1, v/v), and after 30 min a solution of calix[4]arene 30 (1.1 g, 1.1 mmol) in CH₂Cl₂ (5 mL) was added. After the starting material was consumed (TLC, Hex/AcOEt, 7/3, ~1h), the reaction mixture was washed with 10% aq NaHCO₃ (5 mL), brine (5 mL) and dried over MgSO₄, and evaporated in vacuo. The residue was treated with hexane/CH₂Cl₂ (5:1) to give derivative 31 as a colorless solid. Yield 0.83g (95%); mp 174-176 °C; ¹H NMR (CDCl₃): δ 7.33 (m, 10 H), 7.07, 7.00 (2 x d, J = 7.3 Hz, 8 H), 6.91, 6.68 (2 x t, J = 7.3 Hz, 4 H), 4.38 (s, 4 H), 3.87 (AB q, J = 16.9 Hz, 8 H), 3.6 (m, 8 H), 3.30 (t, J = 6.0 Hz, 4 H), 2.91 (t, J = 6.0 Hz, 4 H), 1.68 (br s, 2 H); ¹³C NMR (CDCl₃): δ 156.3, 156.1, 138.4, 133.8, 133.7, 129.5, 129.4, 128.5, 127.9, 127.8, 127.6, 123.2, 123.0, 73.2, 71.4, 68.1, 61.3, 38.0; FTIR (CHCl₃): ν 3529, 3421, 3066, 3033, 2927, 2872, 1468, 1365, 1324, 1247, 1215, 1092, 1037 cm⁻¹; Anal. calcd for C₅₀H₅₂O₈: C, 76.90; H, 6.71. Found: C, 76.82; H, 6.66.

Bis(1-propyloxy)-bis(2-benzyloxy(ethylx)oxy)calix[4]tube (32): 25,27-Bis(2-benzyloxy)-ethylx)oxy)-26,28-bis(2-(hydroxy)ethylx)oxy)calix[4]arene 31 (0.12 g, 0.153 mmol) was dissolved in dry THF (40 mL), and NaH (60% suspension in mineral oil, 0.61 g, 1.5 mmol) was added. The mixture was stirred at 45°C for 1 h, after which a solution of 25,27-bis(2-(p-toluenesulfonyloxy)ethylx)oxy)-26,28-bis(1-propyloxy)calix[4]arene 23⁶⁹ (0.14 g, 0.153 mmol) in THF (20 mL) was added slowly over 4 h.
The reaction mixture was refluxed for 24 h. After cooling, the solvent was evaporated under reduced pressure and CH$_2$Cl$_2$ (30 mL) and 10% aq HCl (10 mL) were added. The organic layer was washed by 10% aq NaHCO$_3$ (10 mL), saturated solution of NaCl (2 x 10 mL), dried over MgSO$_4$ and evaporated in vacuo. The residue was purified by column chromatography with CH$_2$Cl$_2$-MeOH, 99:1 (R$_f$ = 0.3) as an eluent to afford product 32 as a colorless solid. Yield 0.12 g (56%); mp >270°C (decomp.); $^{1}$H NMR (CDCl$_3$): $\delta$ 7.3 (m, 10 H), 7.17, 7.16 (2 x d, $J$ = 7.5 Hz, 8 H), 7.02 (m, 12 H), 6.85, 6.72 (2 x t, $J$ = 7.5 Hz, 4 H), 4.31 (s, 4 H), 3.90 (AB q, $J$ = 16.5 Hz, 8 H), 3.88 (AB q, $J$ = 16.5 Hz, 8 H), 3.56 (m, 8 H), 3.48, 3.31, 2.92 (3 x t, $J$ = 6.5 Hz, 12 H), 2.57 (m, 8 H), 1.06 (m, 4 H), 0.56 (t, $J$ = 7.3 Hz, 6 H); $^{13}$C NMR (CDCl$_3$): $\delta$ 157.3, 156.6, 155.9, 155.8, 134.2, 134.1, 134.0, 129.1, 129.0, 128.9, 128.8, 128.5, 127.7, 127.6, 122.9, 122.8, 122.5, 122.0, 73.1, 71.5, 69.1, 68.5, 68.2, 66.1, 66.0, 38.3, 38.1, 22.7, 10.2; FTIR (CHCl$_3$): v 3065, 3033, 2925, 2875, 1462, 1246, 1427, 1215, 1124, 1094, 1034, 1009 cm$^{-1}$; MALDI-FTMS: m/z (M+Na$^+$) 1363.6439, calcd for C$_{88}$H$_{92}$O$_{12}$Na 1363.6486.

**Bis(1-propyloxy)-bis(2-hydroxy(ethyloxy))calix[4]tube (27):** A mixture of 10 wt % Pd/C (0.03 g), benzylated calix[4]tube 32 (0.06 g, 0.044 mmol) and AcOH (0.1 mL) in THF (5 mL) was stirred under H$_2$ atmosphere (1 atm) at rt until all starting material disappeared (TLC, CH$_2$Cl$_2$-MeOH, 99:1). The suspension was filtered through Celite and the clear solution was concentrated in vacuo. The residue was triturated with MeOH (3 x 2 mL) to afford product 7 as a white powder. Yield 82% (0.042 g, 0.036 mmol); mp >300°C (decomp.); $^{1}$H NMR (CDCl$_3$): $\delta$ 7.21, 7.15 (2 x d, $J$ = 7.6 Hz, 8 H),
7.05 (m, 12 H), 6.95, 6.86 (2 x t, J = 7.6 Hz, 4 H), 3.95 (AB q, J = 17.2 Hz, 8 H), 3.88
(AB q, J = 16.5 Hz, 8 H), 3.63 (t, J = 7.0 Hz, 4 H), 3.56 (m, 8 H), 3.31 (t, J = 7.0 Hz, 4
H), 3.21 (m, 4 H), 2.56 (m, 8 H), 2.27 (br s, 2 H), 1.06 (m, 4 H), 0.56 (t, J = 7.6 Hz, 6
H); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 157.3, 156.4, 156.0, 155.8, 134.2, 134.0, 133.9, 133.5, 129.2,
129.1, 128.9, 128.8, 123.6, 123.0, 122.8, 121.9; FTIR (KBr): \(\nu\) 3529, 3453, 3060, 3030,
3011, 2924, 2875, 1459, 1216, 1132, 1094, 1035, 1011 cm\(^{-1}\); MALDI-FTMS: \(m/z\)
(M+Na\(^+\)) 1183.5426, calcd for C\(_{74}\)H\(_{80}\)O\(_{12}\)Na 1183.5547.

**Bis(1-propyloxy)-bis(2-methyl(ethyloxy))calix[4]tube (27b):** Sodium hydride
(60% suspension in mineral oil, 0.034 mmol) was added to the THF (2 mL) solution of
calix[4]tube 27 (0.010 g, 0.0086 mmol), and the mixture was stirred at rt for 1 h. MeI
(0.0096 g, 0.068 mmol, 0.0040 mL) was added, and the reaction mixture was stirred
overnight. The solvent was removed under reduced pressure, and the residue was
dissolved in CH\(_2\)Cl\(_2\) (5 mL). The organic solution was washed by 10% aq HCl (1 mL),
10% aq NaHCO\(_3\) (1 mL) and dried over MgSO\(_4\). Preparative TLC (SiO\(_2\), Hexanes-
AcOEt, 7:3) was then performed to obtain the dimethylated product. Yield 0.005 g
(49%): \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.19, 7.18 (2 x d, J = 7.3 Hz, 8 H), 7.05 (m, 12 H), 6.93,
6.84 (2 x t, J = 7.3 Hz, 4 H), 3.89 (m, 16 H), 3.57 (m, 12 H), 3.31 (t, J = 7.3 Hz, 4 H),
3.11 (s, 6 H), 2.95 (t, J = 6.0 Hz, 4 H), 2.58 (m, 8 H), 1.06 (m, 4 H), 0.57 (t, J = 7.3 Hz,
6 H); ESI-TOF: \(m/z\) (M+Na\(^+\)) 1211.5855, calcd for C\(_{112}\)H\(_{120}\)O\(_{16}\)Na 1211.5838.
**Bis(1-propyloxy)-bis(2-(p-toluenesulfonyloxy)ethyloxy)calix[4]tube (28):**

Bis(1-propyloxy)-bis(2-hydroxyethyloxy)calix[4]tube 7 (0.11 g, 0.095 mmol), DMAP (0.046 g, 0.38 mmol), and p-toluenesulfonyl chloride (0.070 g, 0.38 mmol) were dissolved in CH$_2$Cl$_2$ (15 mL) and cooled at -5°C. Triethylamine (0.20 mL) was added, and the solution was stirred overnight at rt. The solution was evaporated to dryness, redissolved in CH$_2$Cl$_2$, then washed with 5% HCl, water, and brine. The organic layer was dried with Na$_2$SO$_4$ and evaporated to dryness. Treatment with MeOH produced compound 28 as colorless solid. Yield 0.12 g (88%); mp 242-243 °C; $^1$H NMR (CDCl$_3$): $\delta$ 7.79 (d, $J$ = 8.4 Hz, 4H), 7.40 (d, $J$ = 8.4 Hz, 4H), 7.17, 7.15 (2 x d, $J$ = 1.7 Hz, 8H), 7.06-6.97 (t+d+t, $J$ = 7.5 Hz, 8H), 6.94 (d, $J$ = 7.3 Hz, 4H), 6.86 (t, $J$ = 7.3 Hz, 2H), 6.69 (t, $J$ = 7.3 Hz, 2H), 3.89-3.80 (m, 16H), 3.57 (m, 12H), 3.39 (m, 4H), 3.32 (t, $J$ = 7.3 Hz, 4H), 2.57 (m, 8H), 2.48 (s, 6H), 1.10 (m, 4H), 0.58 (t, $J$ = 7.3 Hz, 6H); $^{13}$C (CDCl$_3$): $\delta$ 157.3, 155.9, 155.8, 155.6, 145.0, 134.2, 134.0, 133.9, 133.8, 133.2, 132.1, 129.1, 129.0, 128.8, 128.0, 123.3, 122.9, 122.8, 121.9, 71.5, 69.1, 68.9, 67.8, 66.8, 66.2, 66.0, 38.3, 38.0, 22.7, 21.7, 10.2; FTIR (KBr): ν 3061, 3031, 3014, 2959, 2918, 2874, 1459, 1214, 1177, 1095, 1033, 1011 cm$^{-1}$; Anal. calcd for C$_{88}$H$_{96}$O$_{16}$S$_2$: C, 71.71; H, 6.57. Found: C, 71.78; H, 6.46.

**Dimeric Tube (15):** A solution of 25, 27-bis(2-hydroxyethyloxy)-26, 28-bis(1-propyloxy)calix[4]arene 22$^{68}$ (0.10 g, 0.16 mmol) and 25,27-bis(2-p-toluenesulfonyloxy-ethyloxy)-26,28-bis(1-propyloxy)calix[4]arene 23$^{99}$ (0.14 g, 0.16 mmol) in THF (25 mL) were added dropwise to a suspension of NaH (60% in mineral
oil, 15 mg, 0.64 mmol) in THF (150 mL) at 70°C over 8 h. The mixture was further refluxed for 24 h, evaporated to dryness, suspended in CH₂Cl₂ (50 mL), and neutralized at 0°C with 5% aq HCl (50 mL). The organic layer was washed with water (3 x 5 mL), dried over Na₂SO₄, and then evaporated to dryness. The residue was treated with MeCN to produce nanotube 15 as a white solid. Yield 0.11 g (55%); mp > 300°C; ¹H NMR (CDCl₃): δ 7.18 (d, J = 7.5 Hz, 8 H), 7.03-6.99 (d + t, 12 H), 6.84 (t, J = 7.5 Hz, 4 H), 3.89 (2 x d, J = 17.0 Hz, 16 H), 3.57 (t, J = 7.0 Hz, 8 H), 3.31 (t, J = 7.0 Hz, 8 H), 2.58 (t, J = 7.5 Hz, 8 H), 1.09-1.05 (m, 8 H), 0.56 (t, J = 7.0 Hz, 12H); ¹³C NMR (C₂D₂Cl₄): δ 157.2, 155.9, 134.2, 134.1, 129.2, 129.0, 122.8, 122.1, 71.7, 69.1, 66.5, 38.3, 22.8, 10.4; FTIR (CCl₄): ν 3063, 3034, 3016, 2961, 2961, 2922, 2875, 1459, 1216, 1128, 1094, 1034, 1011 cm⁻¹; MALDI-FTMS, m/z 1179.5939 [M + Na⁺]; calcd for C₇₆H₈₄O₁₀Na, 1179.5956.

**Trimeric Tube (16):** A solution of 25,26,27,28-tetrakis(2-p-toluenesulfoxyethoxy)-calix[4]arene 26⁷¹ (100 mg, 0.08 mmol) and 25, 27-bis(2-hydroxyethyloxy)-26, 28-bis(1-propyloxy)calix[4]arene 22⁶⁸ (98 mg, 0.16 mmol) in THF (25 mL) were added dropwise to a suspension of NaH (60% in mineral oil, 26 mg, 1.3 mmol) in THF (150 mL) at 70°C over 8 h. The mixture was further refluxed for 24 h, evaporated to dryness, suspended in CH₂Cl₂ (50 mL), and neutralized at 0°C with 5% aq HCl (50 mL). The organic layer was washed with water (3 x 5 mL), dried over Na₂SO₄, and then evaporated to dryness. The residue was treated with MeCN to produce nanotube 16 as a white solid. Yield 0.10g (70%); mp >300°C (decomp.); ¹H
NMR (CDCl₃): δ 7.20, 7.18 (2 x d, J = 7.3 Hz, 16 H), 7.08 (t, J = 7.3 Hz, 4 H), 7.02 (d, J = 7.3 Hz, 8 H), 6.98, 6.85 (2 x t, J = 7.3 Hz, 8 H), 3.94 (s, 8 H), 3.88 (AB q, J = 16.5 Hz, 16 H), 3.57 (m, 16 H), 3.30 (t, J = 7.3 Hz, 8 H), 2.55 (m, 16 H), 1.06 (m, 8 H), 0.56 (t, J = 7.3 Hz, 12 H); ¹³C NMR (C₂D₂Cl₄): δ 157.2, 156.2, 155.9, 134.2, 134.1, 134.0, 129.3, 129.1, 128.8, 122.9, 122.7, 122.0, 71.8, 70.9, 69.2, 66.7, 66.5, 38.3, 38.1, 22.8, 10.4; FTIR (CCl₄): ν 3064, 3033, 3016, 2959, 2921, 2873, 1459, 1216, 1125, 1093, 1035, 1010 cm⁻¹; MALDI-FTMS: m/z [M+Na⁺] 1743.8443, calcd for C₁₁₂H₁₂₀O₁₆Na 1743.8473.

**Tetrameric Nanotube (17):** A solution of bis(1-propoxy)-bis(2-(p-toluene-sulfonyloxy)ethoxy)calix[4]tube 28 (57 mg, 0.039 mmol) and bis(1-propoxy)-bis(2-hydroxyethoxy)-calix[4]tube 27 (45 mg, 0.039 mmol) in THF (25 mL) was added dropwise over 1 hr into a mixture of NaH (60% suspension in mineral oil, 12 mg, 0.31 mmol) and K₂CO₃ (22 mg, 0.16 mmol) in THF (100 mL) at reflux temperature. The mixture was further refluxed for 24 h, evaporated to dryness, suspended in CH₂Cl₂ (50 mL), and neutralized at 0°C with 5% HCl (25 mL). The organic layer was washed with water (2 x 5 mL), dried over Na₂SO₄, and then evaporated to dryness. The residue was treated with MeCN to produce tetracalix[4]tube as a colorless solid. Yield 56 mg (64%); mp >300 °C (decomp.); ¹H NMR (CDCl₃): δ 7.22, 7.19 (2 x d, J = 7.3 Hz, 24 H), 7.07-6.97 (m, 20 H), 6.87 (t, J = 7.3 Hz, 4 H), 3.94 (s, 16 H), 3.88 (AB q, J = 17.5 Hz, 16 H), 3.58 (m, 24 H), 3.28 (t, J = 7.3 Hz, 8 H), 2.58 (m, 24 H), 1.09 (m, 8 H), 0.58 (t, J = 7.3 Hz, 12 H); FTIR (CCl₄): ν 3061, 3032, 3010, 2958, 2925, 2873, 1459, 1216, 1128,
1094, 1033, 1012 cm$^{-1}$; MALDI-TOF MS: $m/z$ (M+Na$^+$) 2308, calcd for C$_{148}$H$_{156}$O$_{22}$Na
2308. No high-resolution mass spectrum can be obtained due to high molecular weight. No good elemental analysis data can be obtained. Similar cases have been reported in literature.\textsuperscript{100,101} There are two possible and widely accepted explanations presented: (1) inclusion of solvent or atmospheric molecules in cavity-possessing compounds, and (2) incomplete combustion of the high-melting compounds under standardized conditions of the elemental analysis.

**Pentameric Nanotube (18):** A solution of 25, 26, 27, 28-tetrakis(2-\textit{p}-toluene-sulfoxyethoxy)-calix[4]arene \textsuperscript{26}\textsuperscript{71} (50 mg, 0.041 mmol) and bis(1-propoxy)-bis(2-hydroxyethoxy)calix[4]tube \textsuperscript{27} (95 mg, 0.082 mmol) in THF (25 mL) was added dropwise over 1 hr into a mixture of NaH (60% suspension in mineral oil, 13 mg, 0.33 mmol) and K$_2$CO$_3$ (22 mg, 0.16 mmol) in THF (100 mL) at reflux temperature. The mixture was further refluxed for 24 h, evaporated to dryness, suspended in CH$_2$Cl$_2$ (50 mL), and neutralized at 0°C with 5% HCl (25 mL). The organic layer was washed with water (2 x 5 mL), dried over Na$_2$SO$_4$, and then evaporated to dryness. The residue was treated with MeCN to produce pentacalix[4]tube \textbf{18} as a colorless solid. Yield 96 mg (82%); mp $>$300°C (decomp.); $^1$H NMR (CDCl$_3$): $\delta$ 7.20, 7.17 (2 x d, $J$ = 7.0 Hz, 32 H), 7.09-6.98 (m, 24 H), 6.87 (t, $J$ = 7.3 Hz, 4 H), 3.94 (s, 24 H), 3.93 (AB q, $J$ = 16.9 Hz, 16 H), 3.62 (m, 32 H), 3.33 (t, $J$ = 7.3 Hz, 8 H), 2.58 (m, 32 H), 1.11 (m, $J$ = 7.3 Hz, 8 H), 0.58 (t, $J$ = 7.3 Hz, 12 H); FTIR (CCl$_4$): $\nu$ 3063, 3033, 3016, 2958, 2926, 2874, 1459, 1217, 1128, 1094, 1033, 1010 cm$^{-1}$; MALDI-TOF MS: $m/z$ (M+Na$^+$) 2872, calcd
for C_{184}H_{192}O_{28}Na 2872. No high-resolution mass spectrum can be obtained due to high molecular weight. No good elemental analysis data can be obtained. Two possible and widely accepted explanations have been presented in literature: (1) inclusion of solvent or atmospheric molecules in cavity-possessing compounds, and (2) incomplete combustion of the high-melting compounds under standardized conditions of the elemental analysis.\textsuperscript{100,101}

**X-ray Crystallography:** X-ray quality crystals of 15, 16 and 31 were obtained from CHCl\textsubscript{3}-CH\textsubscript{3}OH solutions at room temperature. A suitable crystal of 15, 16 or 31 covered with a layer of hydrocarbon oil was selected and mounted with Paratone-N oil on a Cryo-Loop, and immediately placed in the low-temperature nitrogen stream. The X-ray intensity data were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with a Oxford Cryosystems 700 Series cooler, a graphite monochromator, and a Mo K\textsubscript{α} fine-focus sealed tube (\( \lambda = 0.71073 \) Å). The detector was placed at a distance of 5.995 cm from the crystal. The data frames were integrated with the Bruker SAINT-Plus (version 6.45) software package. Data were corrected for absorption effects using the multi-scan technique (SADABS). Structures were solved and refined using Bruker SHELXTL (Version 6.14) software package. Compound 15 crystallizes with two CHCl\textsubscript{3} molecules for each 15 moiety. Solution and refinement proceeded smoothly. Compound 16 crystallizes with 4.5 CHCl\textsubscript{3} molecules in the asymmetric unit. The CHCl\textsubscript{3} molecules show severe disorder. The intensity of high angle data suffers due to this disorder. It also causes significant difficulties during the
refinement stage. Nevertheless, a good data set was collected, and the various disorders were modeled well to bring the overall $\sim R1 = 8\%$. More importantly, nanotube 16 behaves well during the refinement and shows no ill effects as a result of CHCl$_3$ disorder. One of the n-propyl groups of 16 displays minor disorder which was modeled successfully. All the hydrogen atoms were also included during the refinement. For the x-ray data, see pages 143, 148 and 155.

**General Procedure for the Preparation of Nitrosonium Complexes from NO$_2$/N$_2$O$_4$:** In the NMR tube, NO$_2$/N$_2$O$_4$ gas was bubbled for 20 s through a solution of calix[4]tubes (~ 4 mM) and 2 equiv SnCl$_4$ (from 2.8 M stock solution) per calixarene unit in (CDCl$_2$)$_2$, and after homogenization the spectrum was recorded.

**General Procedure for Titration Experiments:** An aliquot from the stock solution of $\tau$-butyl nitrite (2.8 M) in (CDCl$_2$)$_2$ was added to the NMR tube containing solution of calix[4]tubes (~ 4 mM) and 2 equiv of SnCl$_4$ (from 2.8 M stock solution) per calixarene unit in (CDCl$_2$)$_2$ and after homogenization the spectrum was recorded. Additional aliquots of the nitrite were added and the spectrum was recorded after each addition. The concentration of complexes 33 and 34 were determined by integration of the aromatic CH protons and/or the OCH$_2$ methylene protons vs. the corresponding signals of free tubes 15 and 16, respectively.
**FTIR Spectroscopy:** In a general procedure, each compound was dissolved in (CHCl$_2$)$_2$ at 4 \times 10^{-3}$ M, followed by the addition of 2 equiv of SnCl$_4$ and 2 equiv of t-BuONO per calixarene unit. The spectra were recorded in solution, using a NaCl amalgamated sealed cell (1.0 mm) by co-addition of 20 scans, back and forward, at a resolution 4 cm$^{-1}$. For each measurement, the solvent was used for background.

**Biscalix[4]tube-NO$^+$ Complex (33).** $^1$H NMR (CDCl$_2$)$_2$: $\delta$ 7.36 (t, $J = 7.5$ Hz, 4H), 7.26 (d, $J = 7.5$ Hz, 8H), 7.10 (d, $J = 7.5$ Hz, 8H), 6.31 (t, $J = 7.5$Hz, 4 H), 4.24 (m, 8 H), 4.02 (m, 8 H), 3.87 (t, $J = 7.5$ Hz, 8 H), 3.83, 3.64 (2 x d, $J = 14$ Hz, 16 H), 1.9-1.8 (m, 8H), 1.08 (t, $J = 7.5$ Hz, 12 H); UV-vis (CDCl$_2$)$_2$: $\lambda_{\text{max}}$ 525.0 nm; FTIR (CDCl$_2$)$_2$: v 1958 cm$^{-1}$ (NO$^+$).

**Triscalix[4]tube-NO$^+$ Complex (34).** $^1$H NMR (CDCl$_2$)$_2$: $\delta$ 7.35 (m, 20H), 7.11 (d, $J = 7.3$ Hz, 8H), 6.50 (t, $J = 7.3$ Hz, 4H), 6.47 (t, $J = 7.3$ Hz, 4H), 4.30 (m, 16H), 4.06 (m, 16H), 3.86 (m, 24H), 3.66 (d, $J = 14$, 8H), 1.92-1.86 (m, 8H), 1.08 (t, $J = 7.3$ Hz, 12H); UV-vis (CDCl$_2$)$_2$: $\lambda_{\text{max}}$ 524.1 nm; FTIR (CDCl$_2$)$_2$: v 1958, 1940 cm$^{-1}$ (NO$^+$).

**Tetracalix[4]tube-NO$^+$ Complex (35):** $^1$H NMR (CDCl$_2$)$_2$: $\delta$ 7.41-7.09 (m, 36H), 6.62-6.56 (m, 8H), 6.42 (t, $J = 7.5$ Hz, 4H), 4.27 (m, 24H), 4.05 (m, 24H), 3.87 (m, 34H), 3.67 (d, $J = 15.4$ Hz, 8H), 1.91 (m, $J = 7.3$ Hz, 8H), 1.08 (t, $J = 7.3$ Hz, 12H); UV-vis (CDCl$_2$)$_2$: $\lambda_{\text{max}}$ 526.0 nm; FTIR (CDCl$_2$)$_2$: v 1958, 1940 cm$^{-1}$ (NO$^+$).
Pentacalix[4]tube-NO$^+$ Complex (36): $^1$H NMR (CDCl$_2$)$_2$: $\delta$ 7.41-7.08 (m, 44H), 6.67-6.55 (m, 12H), 6.43 (t, $J$ = 7.5 Hz, 4H), 4.27-3.63 (m, 112H), 1.94 (m, $J$ = 7.5 Hz, 8H), 1.08 (t, $J$ = 7.5 Hz, 12H); UV-vis (CDCl$_2$)$_2$: $\lambda_{\text{max}}$ 518.9 nm; FTIR (CDCl$_2$)$_2$: $\nu$ 1958, 1940 cm$^{-1}$ (NO$^+$).
APPENDIX 1

$^1$H and $^{13}$C NMR SPECTRA OF
25,27-BIS(1-PROPYLOXY)-26,28-BIS(2-\textit{TERT-}
BUTYLDIMETHYLSILOXY)ETHYLOXY)CALIX[4]ARENE, \textit{1,3-ALTERNATE} (21)
APPENDIX 2

$^1$H NMR SPECTRUM OF
25,27-BIS(2-HYDROXYETHYLOXY)-26,28-BIS(1-PROPYLOXY)CALIX[4]ARENE, 1,3-ALTERNATE (22)
APPENDIX 3

$^1$H NMR SPECTRUM OF
25,27-BIS(2- P-TOLUENESULFONYLOXYETHYLOXY)-26,28-BIS(1-
PROPYLOXY)CALIX[4]ARENE, 1,3-ALTERNATE (23)
APPENDIX 4

$^1$H NMR SPECTRUM OF
25,26,27,28-TETRAKIS[(ETHOXYCARBONYL)METHOXY]CALIX[4]ARENE,
$1,3$-ALTERNATE (24)
APPENDIX 5

$^1$H AND $^{13}$C NMR SPECTRA OF
25,26,27,28-TETRAKIS(2-HYDROXYETHYLOXY)CALIX[4]ARENE,
$1,3$-ALTERNATE (25)
APPENDIX 6

$^1$H AND $^{13}$C NMR SPECTRA OF
25,26,27,28-TETRAKIS(2-P-TOLUENESULFOXYETHOXY)CALIX[4]ARENE,
$1,3$-ALTERNATE (26)
APPENDIX 7

$^1$H AND $^{13}$C NMR SPECTRA OF
25,27-BIS[(2-BENZYLOXY)ETHYLOXY]-26,28-DIHYDROXYCALIX[4]ARENE,
CONE (29)
APPENDIX 8

$^1$H and $^{13}$C NMR SPECTRA OF
25,27-BIS[(2-BENZYLOXY)ETHYLOXY]-26,28-BIS(2-TERT-BUTYLDIMETHYLSILOXY)ETHYLOXY)CALIX[4]ARENE, $1,3$-ALTERNATE (30)
APPENDIX 9

$^1$H AND $^{13}$C NMR SPECTRA OF
25,27-BIS[(2-BENZYLOXY)ETHYLOXY]-26,28-BIS(2-
HYDROXYETHYLOXY)CALIX[4]ARENE, $^1$A, $^3$-ALTERNATE (31)
APPENDIX 10

$^1$H and $^{13}$C NMR SPECTRA OF
BIS(1-PROPYLOXY)-BIS(2-BENZYLOXYETHYLOXY)CALIX[4]TUBE (32)
APPENDIX 11

$^1$H AND $^{13}$C NMR SPECTRA OF
BIS(1-PROPYOXY)-BIS(2-HYDROXYETHYOXY)CALIX[4]TUBE (27)
APPENDIX 12

$^1$H NMR SPECTRUM OF
BIS(1-PROPYLOXY)-BIS(2-METHYLETHYLOXY)CALIX[4]TUBE (27B)
APPENDIX 13

$^1$H and $^{13}$C NMR SPECTRA OF BIS(1-PROPYLOXY)-BIS(2-(P-TOLUENESULFONYLOXY)ETHYLOXY)CALIX[4]TUBE (28)
APPENDIX 14

$^1$H and $^{13}$C NMR SPECTRA OF DIMERIC CALIX[4]TUBE (15)
APPENDIX 15

$^1$H and $^{13}$C NMR SPECTRA OF TRIMERIC CALIX[4]TUBE (16)
APPENDIX 16

$^1$H NMR SPECTRUM OF TETRAMERIC CALIX[4]TUBE (17)
APPENDIX 17

$^1$H NMR SPECTRUM OF
PENTAMERIC CALIX[4]TUBE (18)
APPENDIX 18

$^1$H NMR SPECTRA OF BISCALIX[4]TUBE-NO$^+$ COMPLEX (33)
APPENDIX 19

$^1$H NMR SPECTRA OF
TRISCALIX[4]TUBE-NO$^+$ COMPLEX (34)
APPENDIX 20

$^1$H NMR SPECTRA OF TETRACALIX[4]TUBE-NO$^+$ COMPLEX (35)
APPENDIX 21

$^1$H NMR SPECTRA OF PENTACALIX[4]TUBE-NO$^+$ COMPLEX (36)
APPENDIX 22

X-RAY CRYSTAL DATA FOR
DIMERIC CALIX[4]TUBE 15• 2 CHCl₃
Formula: C_{78}H_{86}Cl_{6}O_{10}
Crystal System: Monoclinic
Space Group: P 2_1/n
Cell Lengths: a = 17.9825(7) Å, b = 10.6205(4) Å, c = 19.8479(7) Å
Cell Angles: \( \alpha = 90.00^\circ, \beta = 111.7390(10)^\circ, \gamma = 90.00^\circ \)
Cell Volume: 3521.0(2) Å³
Z: 2
Density (calculated): 1.317 Mg/m³
Crystal size: 0.36 x 0.17 x 0.02 mm³
Goodness-of-fit on F²: 1.040
Final R indices [I>2\sigma(I)]: R1 = 0.0397, wR2 = 0.1024
R indices (all data): R1 = 0.0465, wR2 = 0.1077

Bond Lengths for 15•2CHCl₃:

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C25 C26 H26B 109.5
H26B C26 H26C 109.5
Cl3 C39 Cl2 110.64(10)
Cl3 C39 H39 108.1
Cl2 C39 H39 108.1
APPENDIX 23

X-RAY CRYSTAL DATA FOR TRIMERIC CALIX[4]TUBE 16•4.5 CHCl₃
Formula $\text{C}_{116.5}\text{H}_{124.5}\text{Cl}_{13.5}\text{O}_{16}$

Crystal System Triclinic

Space Group P - 1

Cell Lengths $a = 14.7634(6) \, \text{Å}$, $b = 15.2376(6) \, \text{Å}$, $c = 26.4844(11) \, \text{Å}$

Cell Angles $\alpha = 75.9360(10)^\circ$, $\beta = 78.0270(10)^\circ$, $\gamma = 80.0890(10)^\circ$

Cell Volume $5606.9(4) \, \text{Å}^3$

$Z$ 2

Density (calculated) 1.338 Mg/m$^3$

Crystal size $0.31 \times 0.27 \times 0.07 \, \text{mm}^3$

Goodness-of-fit on $F^2$ 1.105

Final R indices [$\sigma(I)$] $R1 = 0.0828$, $wR2 = 0.1667$

R indices (all data) $R1 = 0.1100$, $wR2 = 0.1783$

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APPENDIX 24

X-RAY CRYSTAL DATA FOR
25,27-BIS(2-BENZYLOXYETHYLOXY)-26,28-BIS(2-
HYDROXYETHYLOXY)CALIX[4]ARENE, 1,3-ALTERNATE (31)
Formula: $C_{50}H_{52}O_8$

Crystal System: Triclinic

Space Group: $P\bar{1}$

Cell Lengths: $a = 9.9059(14)$ Å, $b = 17.173(2)$ Å, $c = 25.001(4)$ Å

Cell Angles: $\alpha = 81.553(2)^\circ$, $\beta = 87.810(2)^\circ$, $\gamma = 89.952(2)^\circ$

Cell Volume: $4203.76$ Å$^3$

$Z$: 4

Density (calculated): 1.244 Mg/m$^3$

Goodness-of-fit on $F^2$: 1.028

Final R indices [$I>2\sigma(I)$]: $R1 = 0.0844$, $wR2 = 0.2185$

R indices (all data): $R1 = 0.1323$, $wR2 = 0.2522$

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C21 C22   1.510(7)  C22 C27  1.400(7)
C22 C23   1.400(7)  C23 C24  1.392(7)
C24 C25   1.387(7)  C24 C28  1.514(7)
C25 C26   1.377(8)  C26 C27  1.385(8)
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C33 C34   1.504(11) C34 C39  1.360(11)
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(35) Moralez, J. G.; Raez, J.; Yamazaki, T.; Motkuri, R. K.; Kovalenko, A.; Fenniri,  


BIOGRAPHICAL INFORMATION

Voltaire Guanlao Organo was born in the city of Manila, Philippines. He obtained his Bachelor’s Degree in Chemistry from Adamson University, Manila in 1994. After working in the industry and academe for six years, he pursued his doctoral study at the University of Texas at Arlington in the United States in 2002. He worked with Professor Dmitry M. Rudkevich on calix[4]arene-based synthetic nanotubes. In the summer of 2006, he went to Maryland at the National Cancer Institute of the National Institutes of Health and worked with Dr. Martin W. Brechbiel on monoclonal antibody immunoconjugates for cancer treatment. In December of 2006, he received his doctorate degree in chemistry. He will be moving to Medford, Massachusetts to begin his research career as a postdoctoral associate in the laboratory of Professor Elena Rybak-Akimova at the Chemistry Department in Tufts University. His research interests include supramolecular chemistry and molecular recognition.