

Host–Guest Chemistry

**Supramolecular Features of Calixarene-Based Synthetic Nanotubes\*\***

*Voltaire G. Organo, Alexander V. Leontiev, Valentina Sgarlata, H. V. Rasika Dias,\* and Dmitry M. Rudkevich\**

Filling single-walled carbon nanotubes (SWNTs) with foreign species is a quickly emerging research area.<sup>[1]</sup> The major goal is to enforce filling materials to adopt one-dimensional morphology for nanowiring, transport, and information flow. Other potential applications include the use of SWNTs

[\*] V. G. Organo, Dr. A. V. Leontiev, Dr. V. Sgarlata, Prof. Dr. H. V. R. Dias, Prof. Dr. D. M. Rudkevich  
Department of Chemistry & Biochemistry  
The University of Texas at Arlington  
Arlington, TX 76019-0065 (USA)  
Fax: (+1) 817-272-3808  
E-mail: dias@uta.edu  
rudkevich@uta.edu

[\*\*] V.G.O. and A.V.L. contributed equally to this work. Special thanks to Dr. Iris Thondorf for preliminary calculations. Financial support from the National Science Foundation (awards CHE-0350958 to D.M.R and CHE-0314666 to H.V.R.D.), the Alfred P. Sloan Foundation (D.M.R.), and the Robert A. Welch Foundation (grant Y-1289 to H.V.R.D.) is acknowledged.



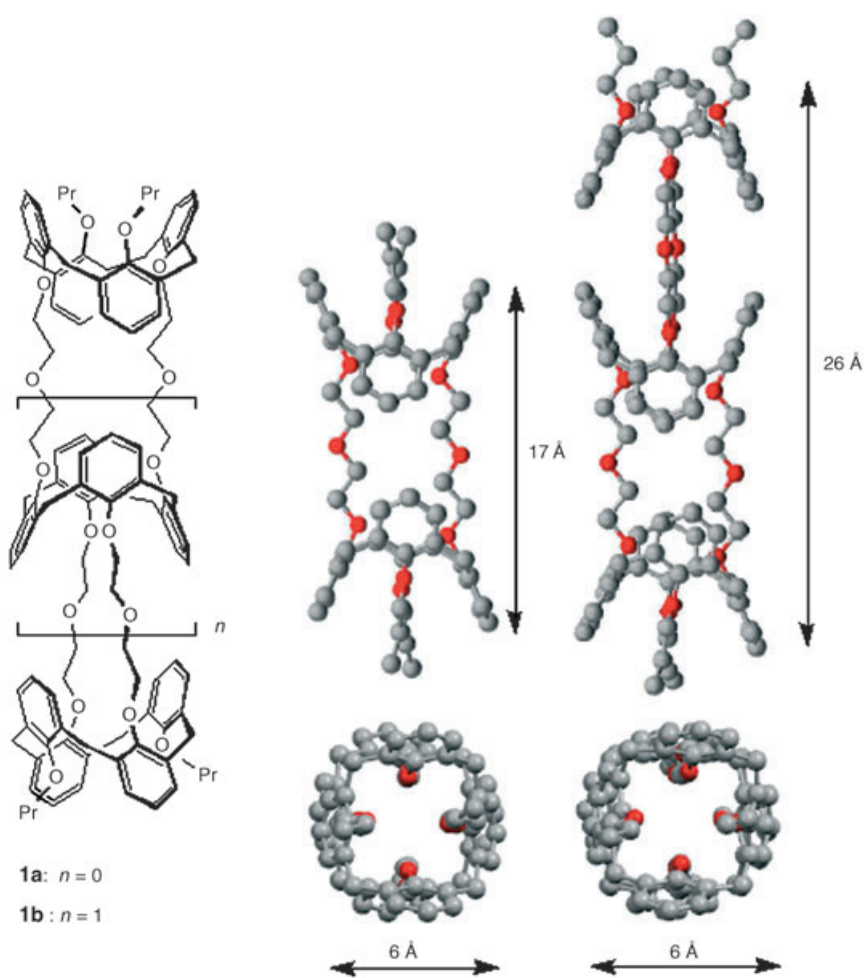
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as reaction vessels and gas-storage cylinders.<sup>[2]</sup> However, far-from-trivial protocols for the chemical opening of SWNTs, still not fully understood mechanisms of their filling, as well as identification of the encapsulated material are some of the problems faced in this area. Physical measurements within the interiors are also a challenge. Synthetic analogues of SWNTs have recently been introduced.<sup>[3,4]</sup> Organic synthesis offers variety of the sizes and shapes. However, most of these synthetic nanotubes are formed through self-assembly and, thus, are stable only under specific conditions. Furthermore, the stability of their encapsulation complexes is generally weak, which diminishes their capabilities as storage and transport devices and materials.

Herein, we demonstrate novel and unique features of synthetic, calixarene-based nanotubes. These nanotubes are covalently built and robust and can be prepared by conventional organic chemistry protocols. The length of the nanotubes can be controlled precisely and easily, and they effectively pack into infinite tubular bundles in the solid state. These nanotubes can also be easily filled and form kinetically and thermodynamically stable encapsulation complexes, and they can be emptied at will in a nondestructive manner. Taken together, we propose reasonable synthetic alternatives to SWNTs for filling.

Earlier we reported that simple calix[4]arenes reversibly interact with  $\text{NO}_2/\text{N}_2\text{O}_4$  and entrap reactive nitrosonium ( $\text{NO}^+$ ) cations— $\text{NO}^+$  is generated upon disproportionation of  $\text{N}_2\text{O}_4$ —within their  $\pi$ -electron-rich interiors, one per cavity.<sup>[5]</sup> Very high association constants  $K_a \gg 10^6 \text{ M}^{-1}$  ( $\Delta G^{295} \gg 8 \text{ kcal mol}^{-1}$ ) for these processes were determined, and the complexes were kinetically stable. These particular properties have been used in the design of calixarene-based nanotubes **1a,b** (Figure 1).

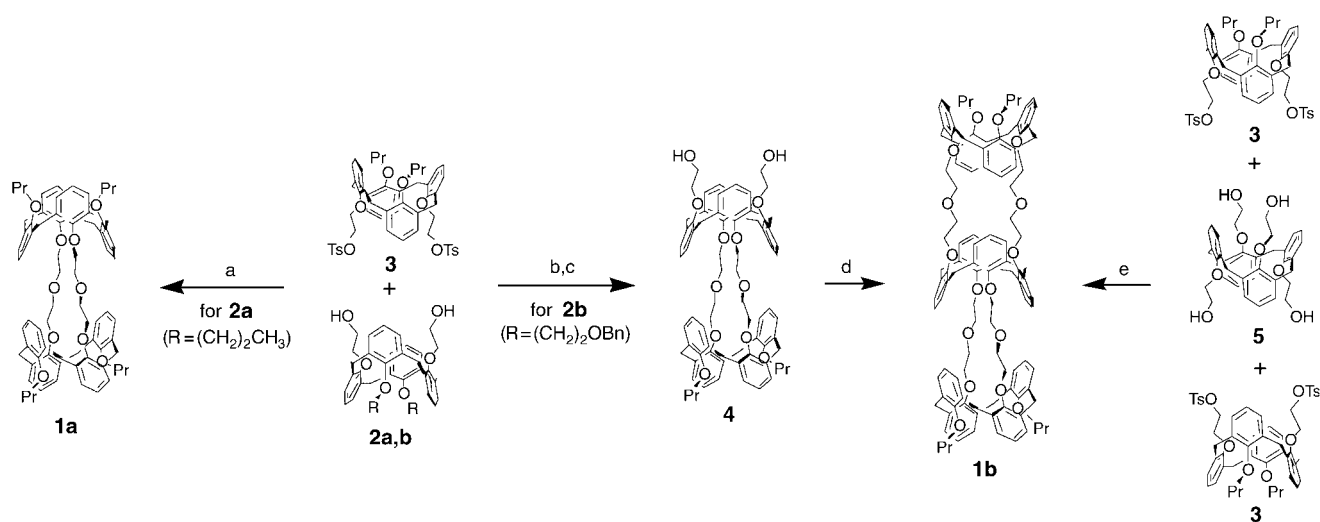
The synthesis of tubes **1a,b** is modular (see Scheme 1 and Supporting Information). Calixarene building blocks were linked by simple, Williamson-type alkylation procedures. Alkylation of calix[4]arene diol **2a** ( $\text{R} = n\text{Pr}$ ) with ditosylate **3** resulted in tube **1a**.<sup>[6]</sup> Reaction of diol **2b** ( $\text{R} = \text{CH}_2\text{CH}_2\text{OBn}$ ) with **3** led to the formation of biscalixarene tube **4**, which has two terminal hydroxyl groups at one end. When **4** was coupled with another equivalent of ditosylate **3**, triscalixarene nanotube **1b** was isolated in 26% yield. Alternatively, nanotube **1b** could be isolated in modest yield ( $\approx 10\%$ ) from the one-step reaction of two equivalents of **3a** with tetrakisalcohol **5**. Nanotubes **1a,b** were characterized by high-resolution  $^1\text{H}$  NMR spectroscopy and COSY



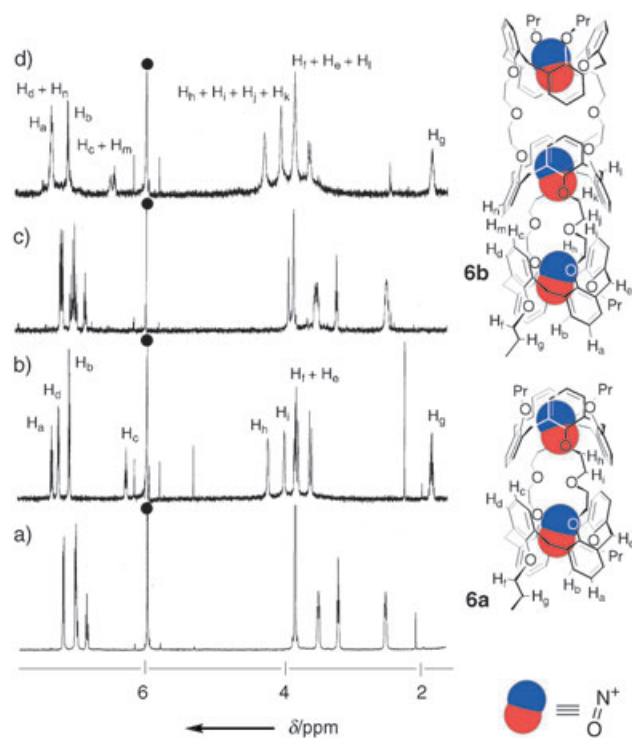
**Figure 1.** Left: Synthetic calixarene-based nanotubes **1a,b** for  $\text{NO}_2/\text{N}_2\text{O}_4$  fixation and nitrosonium ion ( $\text{NO}^+$ ) storage. Right: X-ray crystal structures of **1a,b** (from  $\text{CHCl}_3/\text{MeOH}$ ; side and top views; O red, C gray). Hydrogen atoms are omitted for clarity.

and NOESY experiments, mass spectrometry, and X-ray crystallography.<sup>[7]</sup> X-ray data show that in nanotubes **1a** and **1b**, 1,3-alternate calix[4]arenes are rigidly linked with diethylene glycol bridges to form hollow cylinders with cavities of diameters of approximately 6 Å and lengths of 17 and 26 Å, respectively (Figure 1). The inner tunnels are defined by two cofacial pairs of aromatic rings oriented orthogonally along the cavity axis.

Nanotubes **1a,b** can be easily filled, as each calixarene unit can accommodate one  $\text{NO}^+$  guest. Addition of excess  $\text{NO}_2/\text{N}_2\text{O}_4$  to **1a,b** in tetrachloroethane in the presence of Lewis acids such as  $\text{SnCl}_4$  or  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  resulted in quantitative formation of nitrosonium complexes **6a,b** (Figure 2). Similar complexes formed when nanotubes **1a,b** were mixed with nitrosonium salt  $\text{NO}^+\text{SbF}_6^-$  in tetrachloroethane. Adducts **6a,b** were identified by UV/Vis and  $^1\text{H}$  NMR spectroscopy and exhibit typical features of earlier described, simpler calix[4]arene- $\text{NO}^+$  species.<sup>[5,8]</sup> Of particular importance is the characteristic deep purple color. The broad charge-transfer absorption bands that account for the color are observed at  $\lambda_{\text{max}} \approx 550 \text{ nm}$  in the UV/Vis spectra. Charge transfer only occurs when  $\text{NO}^+$  guests are tightly entrapped inside the



**Scheme 1.** a) NaH, DMF, 80°C, 48 h, 15–20%; b) NaH, THF, reflux, 24 h, 32%; c) H<sub>2</sub>, 10% Pd/C, THF/AcOH, 82%; d) NaH, THF, reflux, 24 h, 26%; e) NaH, THF, reflux, 3 days, 7%. Ts = *p*-toluenesulfonyl; Bn = benzyl; DMF = *N,N*-dimethylformamide.



**Figure 2.** Partial <sup>1</sup>H NMR spectra (500 MHz, (CDCl<sub>2</sub>)<sub>2</sub>, 295 K) of a) nanotube **1a**, b) filled nanotube **6a**, c) nanotube **1b**, and d) filled nanotube **6b**. The residual solvent signals are marked with filled circles (●). The assignments were performed by COSY and NOESY experiments and supported by molecular modeling (MacroModel 7.1).

calixarene cavities.<sup>[5,8,9]</sup> Accordingly, the filling process can be monitored visually.

Upon stepwise addition of NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> or NO<sup>+</sup>SbF<sub>6</sub><sup>−</sup> in [D<sub>2</sub>]tetrachloroethane, signals for the protons of **1a,b** and **6a,b** can be seen separately and in slow exchange by <sup>1</sup>H NMR spectroscopy. This is typical for host–guest complexes with high exchange  $\Delta G^\ddagger$  barriers (> 15 kcal mol<sup>−1</sup>) and/or high values of association constants ( $K_a > 10^6$  M<sup>−1</sup>). The presence

and location of the guests inside nanotubes **6a,b** can be deduced from conventional NMR analysis. Structural fragments that are involved in the complexation process were identified by <sup>1</sup>H NMR spectroscopy, COSY, and NOESY experiments. Although entrapped NO<sup>+</sup> species cannot be directly seen, chemical shifts of the methylene protons from Ar–O–CH<sub>2</sub> and, to a lesser extent, Ar–O–CH<sub>2</sub>CH<sub>2</sub> and the aromatic protons are very sensitive to the encapsulation. Indeed, besides the charge transfer, strong cation–dipole interactions between the oxygen atoms of the calixarenes and the entrapped NO<sup>+</sup> take place.

The three signals for the propyloxy groups in **6a,b** appeared significantly downfield ( $\Delta\delta \approx 1$  ppm) relative to empty tubes **1a,b** (Figure 2). This implies that two NO<sup>+</sup> cations are located at the ends of the nanotubes and occupy the terminal calixarene compartments. The middle calixarene in the longer tube **6b** is most probably filled as well. Downfield shifts ( $\Delta\delta > 1$  ppm) of the corresponding signals for the protons of Ar–O–CH<sub>2</sub> and CH<sub>2</sub>–O–CH<sub>2</sub> were observed for this fragment. Higher stoichiometries of NO<sup>+</sup> were ruled out; there is simply no room to accommodate a larger number of electrostatically repulsive cations.

According to molecular modeling studies, the nitrosonium-filled nanotubes adopt somewhat shrunken structures, with all-*gauche* conformations about the glycol C–C bonds. Such folding brings closer the aromatic rings from the neighboring calixarene units. This behavior was confirmed by NOESY for the nitrosonium-filled nonsymmetrical *O,O'*-dimethylated derivative of **4**. Consequently, the aromatic protons CH<sub>c</sub> of tube **6a**, and CH<sub>c</sub> and CH<sub>m</sub> in tube **6b**, appear shielded and are seen somewhat upfield at  $\delta \approx 6.2$ –6.4 ppm (Figure 2).

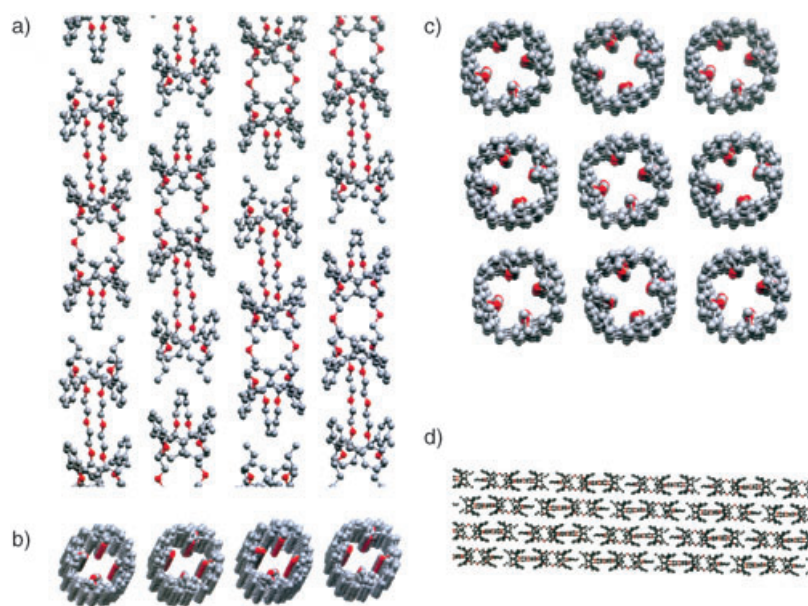
Judging from the <sup>1</sup>H NMR spectra at room temperature, complexation with NO<sup>+</sup> does not influence the symmetry of **6a,b** relative to empty **1a,b**. Although in both cases the nonequivalence of the CH<sub>2</sub> protons of the calixarene methylene bridges becomes more pronounced, the number of <sup>1</sup>H NMR signals for the propyl ArOCH<sub>2</sub>, glycol CH<sub>2</sub>OCH<sub>2</sub>

and  $\text{ArOCH}_2$ , and aromatic groups for **6a,b** does not change and implies that the  $\text{NO}^+$  guests, with van der Waals dimensions of approximately 2 Å, freely rotate along the N–O axis and also tumble within the cavity.

To determine the mechanism of filling is a difficult task<sup>[1]</sup> and it remains a great challenge for SWNTs, but conventional NMR spectroscopy provides useful insights for synthetic tubes such as those prepared here. Modeling suggests that the first  $\text{NO}^+$  ion can enter the nanotube through either its neck or one of the middle gates between the calixarenes. Upon addition of  $\text{NO}^+\text{SbF}_6^-$  to tube **1a**, the intermediate half-filled 1:1 complex **1a-NO<sup>+</sup>** was initially observed and isolated, and the guest was found to be located between the calixarenes, within the electron-rich oxygen atoms of the crown ether.<sup>[6]</sup> The signals for the protons of the propyl Ar–O–Pr group in this complex were not shifted, which indicates that the ends of the nanotube were not occupied with  $\text{NO}^+$ . Likewise upon addition of  $\text{NO}^+\text{SbF}_6^-$  to longer nanotube **1b** (at  $-20^\circ\text{C}$ ), the intermediate partially filled species were observed. They exhibit distinct signals of all groups of protons, but the signals for the propyl Ar–O–Pr protons were not shifted downfield. These intermediate complexes were further converted into **6a,b** simply by addition of more  $\text{NO}_2/\text{N}_2\text{O}_4$  or  $\text{NO}^+\text{SbF}_6^-$ . To avoid electrostatic repulsions, the next  $\text{NO}^+$  ion should instead enter through the neck thus further pushing the first guest towards the end of the tube.

Filled nanotubes **6a,b** are stable in anhydrous solution at room temperature for hours, but can be readily destroyed with  $\text{H}_2\text{O}$  to quantitatively regenerate free **1a,b** (according to  $^1\text{H}$  NMR and UV/Vis spectral analysis). We found that the encapsulated  $\text{NO}^+$  species can also be removed by simple addition of 18-crown-6; it is known that crown ethers form stable complexes with  $\text{NO}^+$ .<sup>[10]</sup> When 18-crown-6 ( $\approx 10$  equiv) was added to solutions of **6a,b** in  $[\text{D}_2]$ tetrachloroethane, empty nanotubes **1a,b** were regenerated within minutes (NMR, UV/Vis), and the deep purple color disappeared. This observation is important, as in this case foreign species are removed without decomposition and without the need to change the polarity of the solution.

Nanotube units **1a** and **1b** pack head-to-tail in straight rows to result in infinitely long cylinders. Chloroform molecules occupy the vacant spaces between the tubes. Nanotube **1b** shows a particularly appealing supramolecular structure (Figure 3) with the neighboring nanocylinders aligned parallel to each other. In each nanocylinder, molecules **1b** are twisted by  $90^\circ$  relative to each other, and the Ar–O–Pr propyl groups effectively occupy the voids between the adjacent molecules. In such an arrangement, the intermolecular distance between two neighboring tubes in the nanocylinder is around 6 Å, and the nanocylinders are separated from each other by about 9 Å. This supramolecular order comes with the tube length and is without precedent for



**Figure 3.** Side and top views of supramolecular packing of nanotube **1b** into infinite nanocylinders and the parallel stacking of neighboring nanotubes. View (d) shows the continuous tunnel of four columns of nine **1b** molecules.

conventional, shorter calixarenes. The unique linear nanostructures maximize the intermolecular van der Waals interactions in the crystal through the overall shape simplification.

In conclusion, besides SWNTs, synthetic nanotubes are now available that pack in tubular bundles and can be reversibly filled with guest molecules. At this stage only certain guests can fill the interiors, but they are charged, which is important for the design of nanowires. Given the ability of calixarenes to react with  $\text{NO}_x$  gases even in the solid state,<sup>[5,11]</sup> we will look at the flow of nitrosonium ions along the infinite nanocylinders in the solid-state bundles of **1a,b**. Not only would the charge be transported and detected through the changes in conductivity, but also the color of the crystals would serve as an indicator of such transport processes.<sup>[12]</sup>

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