A procedure for filling calixarene nanotubes†

Valentina Sgarlata, Voltaire G. Organo and Dmitry M. Rudkevich*

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Alkyl nitrites readily transfer nitrosonium into calixarene-based synthetic nanotubes thus offering a mild, effective and precise method to fill them.

In this communication, we describe a convenient chemical procedure for filling synthetic nanotubes with ionic species. Filling nanotubes with foreign guests leads to the unique, one-dimensional state of matter and may also be useful for nanowiring, charge transport and information flow.[1] Single-walled carbon nanotubes (SWNTs) are difficult to fill, and it is not trivial to quantify and monitor the guest behavior inside. We recently introduced calixarene nanotubes as synthetic alternatives to SWNTs for filling purposes.[2,3] These nanotubes are covalently built and robust. Their length can be controlled precisely through conventional synthetic protocols. They effectively pack into infinite tubular bundles in the solid state. Using NO_2/N_2O_4 gases we filled these nanotubes with multiple nitrosonium (NO^+) guests species and followed the process by conventional spectroscopic techniques in solution.[2] The method described here is easy and precise. It utilizes alkyl nitrites (AlkO–N=O) as a mild source of NO^+. Alkyl nitrites are known as effective NO donors in medicine and they are also nitrosating agents.[4] We have now discovered that NO^+ can be quantitatively transferred from alkyl nitrites into calixarene molecular cages and nanotubes (see **1–3**, Fig. 1).

In contrast to aggressive NO_2/N_2O_4 gases, which are difficult to handle in small, precise quantities and which react with nanotubes upon standing, alkyl nitrites are stable, non volatile liquids. They are easy to transfer by conventional laboratory pipettes. More important, however, is that the proposed procedure allows for the stoichiometric filling of nanotubes and may also be applied to other calixarene-based molecular containers.

Preliminary experiments started with simple calix[4]arenes. Addition of either *n*-butyl or *tert*-butyl nitrite to the $CDCl_3$ solution of tetrakis(*O*-*n*-hexyloxy)calix[4]arene **1** in the presence of 4 eq. of $SnCl_4$, a Lewis acid, led to the rapid, quantitative formation of calixarene–NO^+ complex **4** (Fig. 1).‡,§ Adduct **4** and other similar complexes of calixarenes are known.[5,6] In these, NO^+ is tightly encapsulated inside a π-electron rich calix[4]arene tunnel with a remarkably high $K_{\mathrm{assoc}} > 10^6\ M^{-1}$. Calixarene–nitrosonium complexes were originally prepared from calix[4]arenes and nitrosonium salts,[5,6] calix[4]arenes and NO_2/N_2O_4,[6] or calix[4]-arene cation radicals and free NO[5] and fully characterized by UV-vis, IR, NMR spectroscopy, X-ray crystallography and CHN analysis.

Upon nitrosonium transfer from butyl nitrites, the ^1H NMR spectrum of **4** showed new sets of the calixarene signals, which are clearly distinguished from free calixarene **1** (Fig. 2).

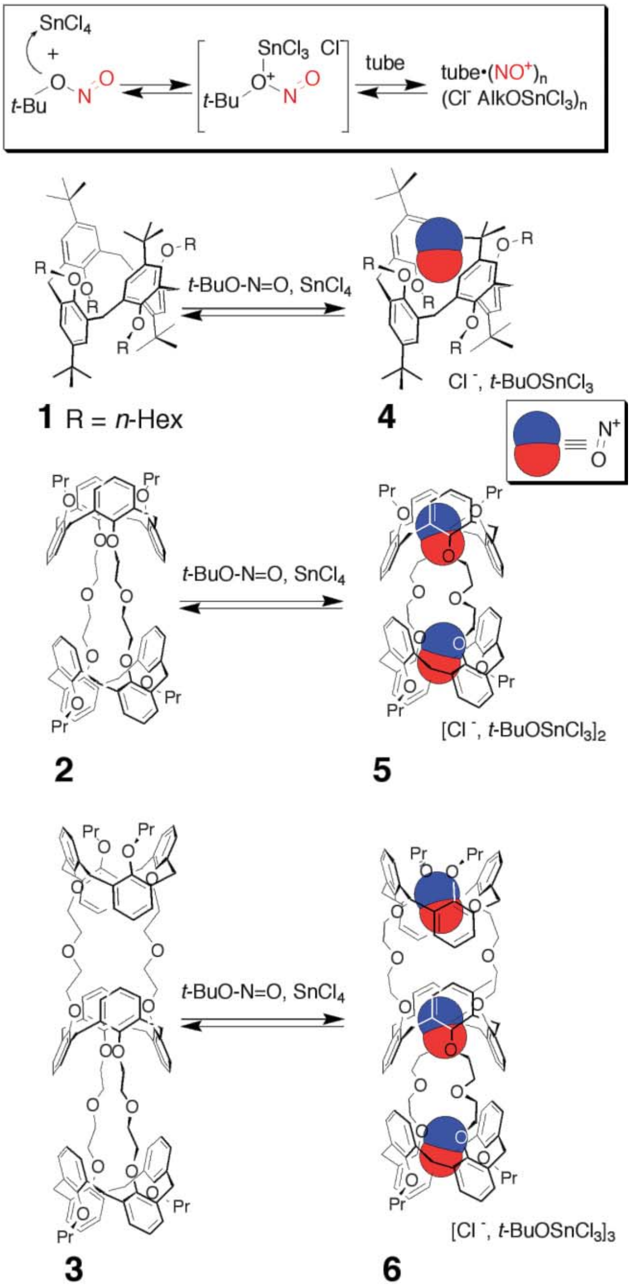

Fig. 1 Filling synthetic nanotubes **2** and **3** through supramolecular nitrosonium transfer.

Department of Chemistry & Biochemistry, The University of Texas at Arlington, Arlington, TX, USA. E-mail: rudkevich@uta.edu; Fax: 1 817 272 3808; Tel: 1 817 272 5245

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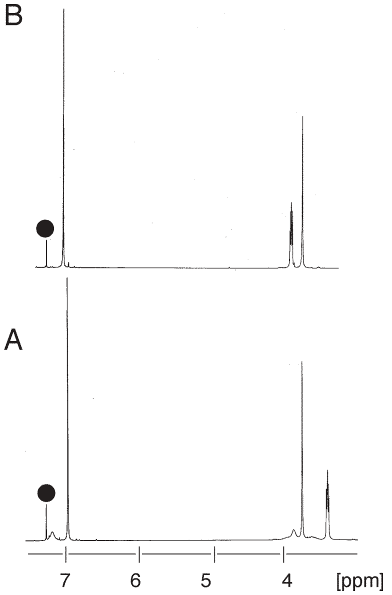

Fig. 2 Portions of the ^{1}H NMR spectra (500 MHz, $CDCl_3$, 295 $\pm$ 1 K) of: A. Calix[4]arene **1** and 4 eq. of $SnCl_4$. B. Calix[4]arene–nitrosonium complex **4** prepared from **1**, 1 eq. of *tert*-butyl nitrite and 4 eq. of $SnCl_4$. The residual $CHCl_3$ signals are marked "•".

In the presence of $SnCl_4$ in $CDCl_3$ the aromatic protons of free **1** were recorded as a singlet at 7.00 ppm. In nitrosonium complex **4**, it was transformed into a singlet at 7.02 ppm. The methylene bridge CH_2 protons of **1** were seen as a singlet at 3.74 ppm. In complex **4**, this was observed at 3.61 ppm. The OCH_2 protons in **1** were recorded at 3.39 ppm, and they moved to 3.77 ppm in complex **4**. Upon stepwise addition of *n*-butyl or *tert*-butyl nitrite to calixarene **1** in $CDCl_3$, ^{1}H NMR signals of **1** and **4** were seen in slow exchange. This is typical for host–guest complexes with high exchange $\Delta G^{\ddagger}$ barriers (>15 kcal/mol) and/or high $K_{\text{assoc}} > 10^6$ M^{-1} values. Importantly, only *one equivalent* of *n*-butyl or *tert*-butyl nitrite is needed to fill the calixarene cavity. Further addition of the nitrite did not change the NMR spectrum.

The NO^+ transfer does not occur in the absence of $SnCl_4$.‡ Most probably, the Lewis acid interacts with the nitrite C–O–N oxygen atom and facilitates breaking the O–N bond (Fig. 1, top). It may also stabilize complex **4** by coordinating to the counter ion, similar to known arene–nitrosonium nitrate complexes.[7] Nitrosation with alkyl nitrites typically follows a concerted mechanism, involving both nitrites and nucleophiles, and free NO^+ species never form. Our case is obviously different.[8]

As the result of charge-transfer, complex **4** is deeply colored. The UV-vis spectrum showed broad charge-transfer band at $\lambda_{\max} \sim 580$ nm, which is characteristic[9] for aryl–NO^+ complexes. At the same time, the solution becomes colorless upon addition of water or large quantities of alcohol. Under these conditions the complex dissociates and releases NO^+.

Addition of *tert*-butyl nitrite and $SnCl_4$ to nanotubes **2** and **3** in $(CDCl_2)_2$ resulted in the rapid formation of nitrosonium filled species **5** and **6**, respectively (Fig. 1).¶ These were identified by NMR and UV-vis spectroscopy, showing similar features with the previously described filled tubes.[2] Due to the strong charge-transfer and ion–dipole interactions, chemical shifts of the Ar–O–CH_2, the Ar–O–CH_2CH_2 and the aromatic protons are sensitive to the NO^+ encapsulation. For example, the propyl Ar–O–CH_2 protons in **5** and **6** were seen significantly down field ($\Delta\delta \sim 1$) compared with empty tubes **2** and **3**. This implies that two NO^+ cations are located at the ends of the nanotubes, occupying the terminal calixarene compartments. Down field shifts ($\Delta\delta > 1$) of the Ar–O–CH_2 and CH_2–O–CH_2 protons of the middle calixarene in tube **3** were also observed.

Upon stepwise addition of *tert*-butyl nitrite and $SnCl_4$ to **2** and **3** in $(CDCl_2)_2$, the ^{1}H NMR signals of free and filled nanotubes were seen separately and in slow exchange (Fig. 3 and Fig. 4). From the integration, it was possible to quantitatively estimate the concentration of complexes **5** and **6**. Two equivalents of *tert*-butyl nitrite were needed to fill biscalixarene tube **2**, and adding three equivalents of the nitrite completely filled triscalixarene nanotube **3**. Further addition of the nitrite did not change the NMR spectra. This confirms the stoichiometry of complexes **5** and **6**, which thus possess two and three NO^+ cations, respectively, one NO^+ per each calixarene unit. The same filled tubes **5** and **6** were independently prepared from **2** and **3**, respectively, by using excess NO_2/N_2O_4 gases in the presence of $SnCl_4$ (see Fig. 3E and Fig. 4E).

In conclusion, nitrosonium cations can be quantitatively released from simple alkyl nitrites into π-electron rich calixarene cavities in the presence of a Lewis acid. This supramolecular reaction can be used to fill calixarene nanotubes with ions for

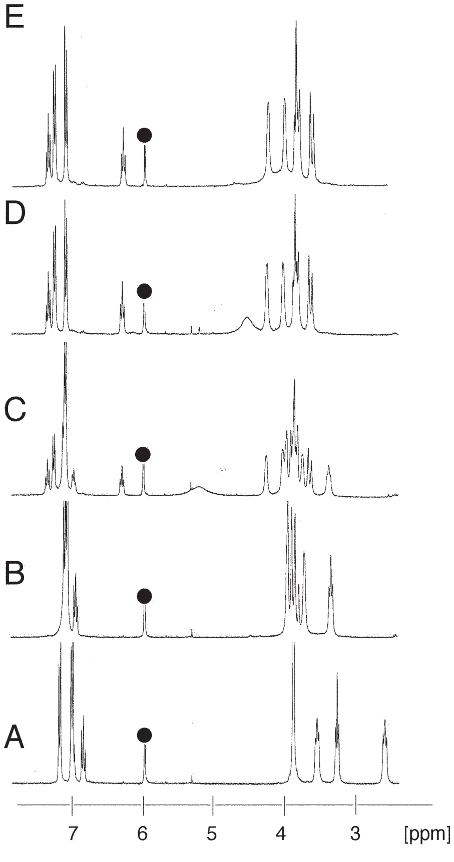

Fig. 3 Portions of the ^{1}H NMR spectra (300 MHz, $(CDCl_2)_2$, 295 $\pm$ 1 K) of: A. Tube **2**. B. Tube **2** and ~ 5 eq. $SnCl_4$. C. Same as B with 1 eq. *tert*-butyl nitrite. D. Same as B with 2 eq. *tert*-butyl nitrite. E. Complex **5** prepared from **2** and excess NO_2/N_2O_4 in the presence of $SnCl_4$. The experiments were performed at least in duplicate showing good reproducibility. The residual $(CHCl_2)_2$ signals are marked as before.

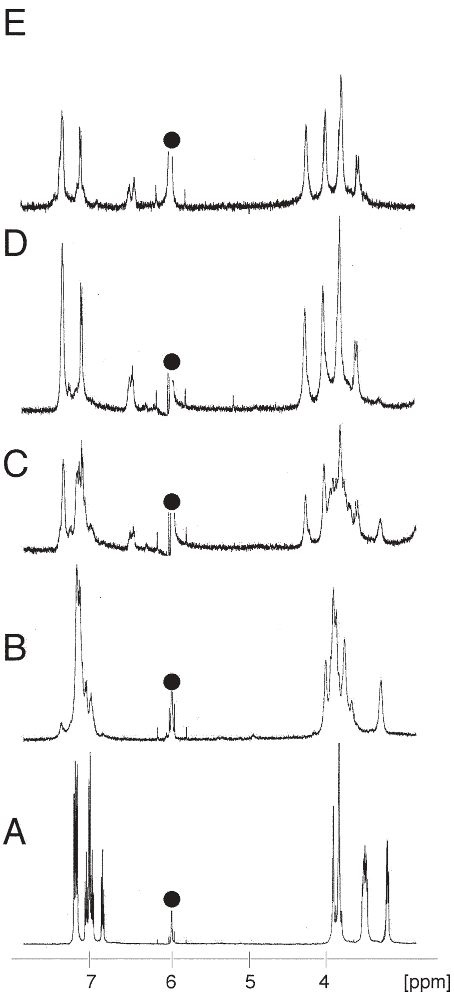

Fig. 4 Portions of the ^{1}H NMR spectra (500 MHz, $(CDCl_2)_2$, 295 ± 1 K) of: A. Nanotube **3**. B. Nanotube **3** and ∼6 eq. $SnCl_4$. C. Same as B with 1.7 eq. *tert*-butyl nitrite. D. Same as B with 3 eq. *tert*-butyl nitrite. E. Complex **6** prepared from nanotube **3** and excess NO_2/N_2O_4 in the presence of $SnCl_4$. The experiments were performed at least in duplicate and showed good reproducibility. The residual $(CHCl_2)_2$ signals are marked as before.

nanowiring and also estimate stoichiometries of their host–guest complexes. Generated from alkyl nitrites and calixarenes complexes may also be employed for storage of active nitrosonium and act as size-shape selective nitrosating reagents.[10] We are now preparing even longer nanotubes and will use alkyl nitrites to fill them. It would be interesting to study spectroscopic features of multiple nitrosonium guests aligned in one dimension. We are also testing the ability of other NO donors to transfer nitrosonium into calixarenes and nanostructures derived from them.

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Notes and references

‡ When smaller quantities of $SnCl_4$ were used, equilibrium between **1** and **4** was established, and comparable amounts of **1** and **4** were detected by ^{1}H NMR spectroscopy. In the subsequent experiments only excess of $SnCl_4$ was used.

§ At this stage, the fate of the *n*-butoxide or *tert*-butoxide anion has not been established. Most probably, it replaces one of the chloride atoms in $SnCl_4$. For reactions between similar Lewis acids and alkyl nitrites, see: ref. 11.

¶ The synthesis of nanotube **3** has now been modified, and 70% yield was obtained for the last coupling step. See the ESI† for details.

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