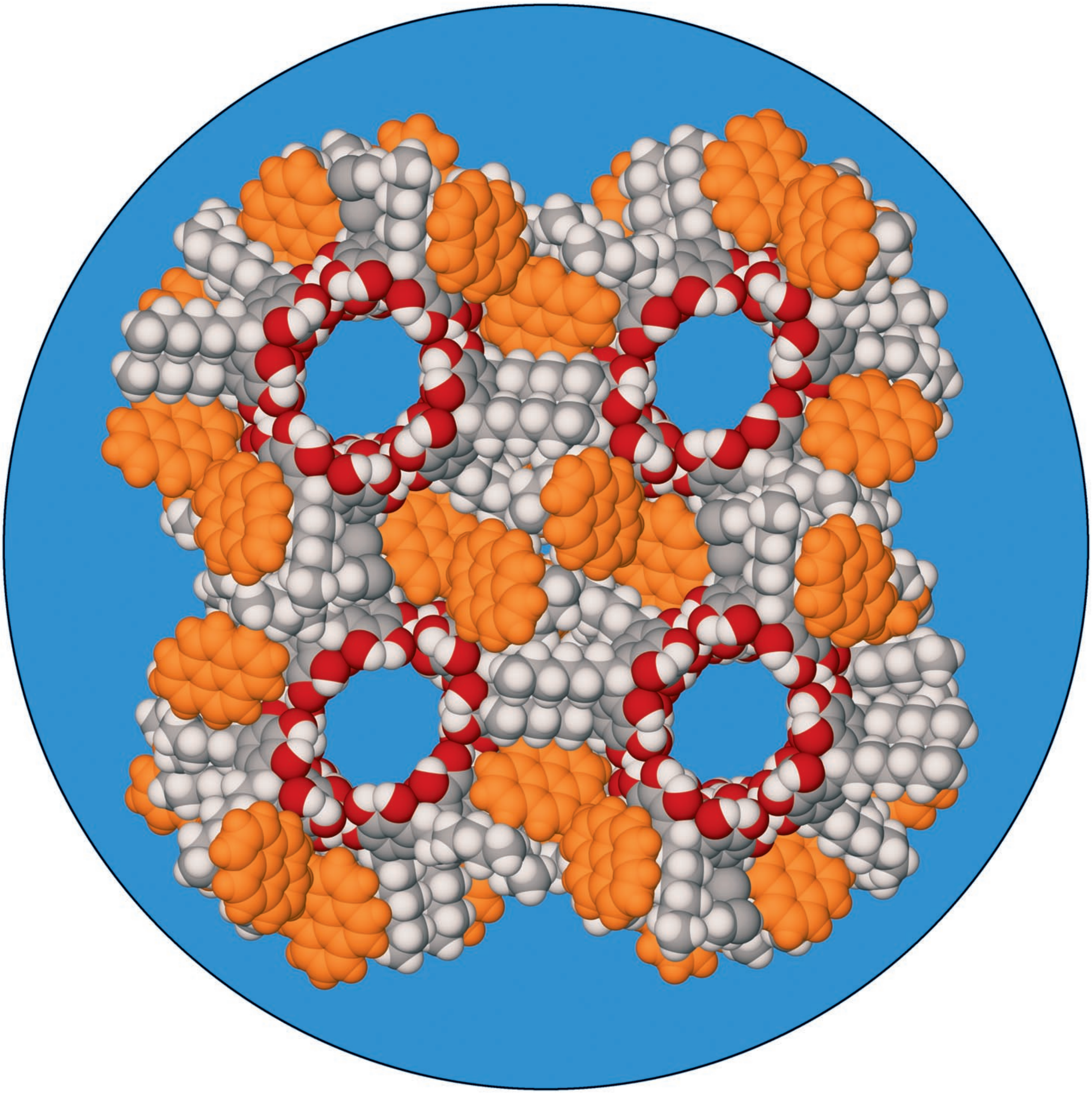
Zuschriften

DOI: 10.1002/ange.200503035



Spheroide Aggregate von *C*-Hexylpyrogallo[4]arenen werden durch Ultraschallbehandlung und Cokristallisation mit Pyren (oder 1-Brompyren) aus wasserhaltigem Acetonitril in organische Nanoröhren mit ähnlichem Innendurchmesser umgewandelt. Weitere Informationen liefert die Zuschrift von J. L. Atwood et al. auf den folgenden Seiten.

Nanostructures

DOI: 10.1002/ange.200503035

Toward the Isolation of Functional Organic Nanotubes**

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The discoveries of buckminsterfullerene (C_{60}) and single-walled carbon nanotubes (SWNTs) represent two very significant advances in the last two decades.[1,2] Both types of material have found utility in important areas such as superconductivity and molecular electronics.[3] Whilst the synthesis and functionalization of carbon nanotubes is now developing rapidly, the materials produced are often costly, irregular in shape, and are typically found to aggregate in large bundles, thus making manipulation somewhat less than straightforward.

Given the intense focus on buckyballs and SWNTs, it is surprising that significantly less efforts have been directed to developing the synthesis of alternative multicomponent organic nanospheres and tubules. Such molecular arrangements present the opportunity for the encapsulation or hosting of suitable guest species within the large resultant internal cavities or channels and also show vast potential for use in the nanotechnology industry. A major problem associated with this goal is that of achieving control over the many intermolecular interactions that stabilize such supramolecular assemblies. Such control has been achieved to some extent with *p*-sulfonatocalix[4]arene, 12 molecules of which can be controlled to assemble around the vertices of nanometer-scaled icosahedra or cuboctahedra.[4,5] The resultant supramolecular geometries are dependent upon both the guest molecules and the metal counterions employed, but both have substantial internal cavity volumes in the 1000–1500 Å^3 range. Additionally, variation of the reaction conditions can result in the formation of related nanotubules, the diameters of which are similar to those of the nanospheroids.

To the best of our knowledge—and without considering, for example, the channels found in zeolites or engineered porous crystals—only a limited number of purely organic nanotubes that have large internal channel volumes have been reported to date.[6,7] The majority of these nanotubes were formed through the self-assembly of cyclic oligomers composed of peptides,[6a] ureas,[6b] or carbohydrates.[6c] Artzner and co-workers documented the remarkable self-assembly of an octapeptide into nanotubes with dimensions that approach those of viral capsids in both solution and the solid state.[7] However, in the context of the present study, an important example of a multicomponent organic nanotube was that formed by the back-to-back solid-state assembly of calix[4]hydroquinone.[8] The crystalline assembly was stabilized by π-stacking interactions between adjacent calixarene moieties. Although these channels could be used to form ultrathin silver nanowires it is difficult to envisage a point at which the assembly could maintain both structure and function in the solution phase.

Six molecules of *C*-methylresorcin[4]arene (**1**) and eight molecules of water self-assemble into a purely organic spheroid of nanometer dimensions that is stabilized by a large number of hydrogen-bonding interactions between the hydroxy groups on the upper rim of the calixarene units and water molecules at the seams of the nanospheroid.[9] Mattay and co-workers described the self-assembly of *C*-isobutylpyrogallol[4]arene into a hexameric capsule arrangement which is reminiscent of that formed with **1**.[10] Some of our recent work has focused on the organization of guest molecules with nanospheroids composed of *C*-alkylpyrogallol[4]arenes **2** whilst also establishing quantitative and reproducible recrystallization procedures from a particular solvent (ethyl acetate).[11,12] Also, solution-phase studies for nanospheroids of **1** and **2** have been developed and scrutinized through a number of spectroscopic techniques to demonstrate the stability of these assemblies in a variety of solvents.[9,13–19] Given that the “footprint” of an SWNT is approximately equal to the diameter of a buckyball[1,2] and that a similar phenomenon is observed with the above-mentioned *p*-sulfonatocalix[4]arene nanospheroids and nanotubules,[4,5] we reasoned that it should be possible to form a purely organic nanotube (from either **1** or **2**) that would be of similar diameter to the corresponding nanospheroids. This is indeed the case for **2**, at least, and we show herein that sonication can be used to construct organic nanotubes that show the possibility for existence and function in the solution phase.

Sonication of a hot solution of *C*-*n*-hexylpyrogallol[4]-arene (PgC6, **3**) and pyrene (**4a**) (or 1-bromopyrene (**4b**)) in acetonitrile/water, followed by cooling of the solution and slow solvent evaporation overnight resulted in the growth of large single crystals of **5** that were suitable for diffraction studies (Figure 1).[20–22] The resolved structure shows the asymmetric unit of **5** to comprise two molecules of PgC6 (**3**) and two molecules of pyrene, as well as a total of 4.5 molecules of acetonitrile and 5.5 molecules of water.

Symmetry expansion of the asymmetric unit shows that the calixarene units form cyclic or disclike tetramers through eight crystallographically unique hydrogen bonds (O···O distances range from 2.702–2.916 Å). These tetramers link together in a tubular fashion through six crystallographically unique interdisc hydrogen-bonding interactions (O···O distances range from 2.742–3.010 Å; Figure 1), with each tetramer being rotated by approximately 45° relative to an axis

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[**] We thank the NSF for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

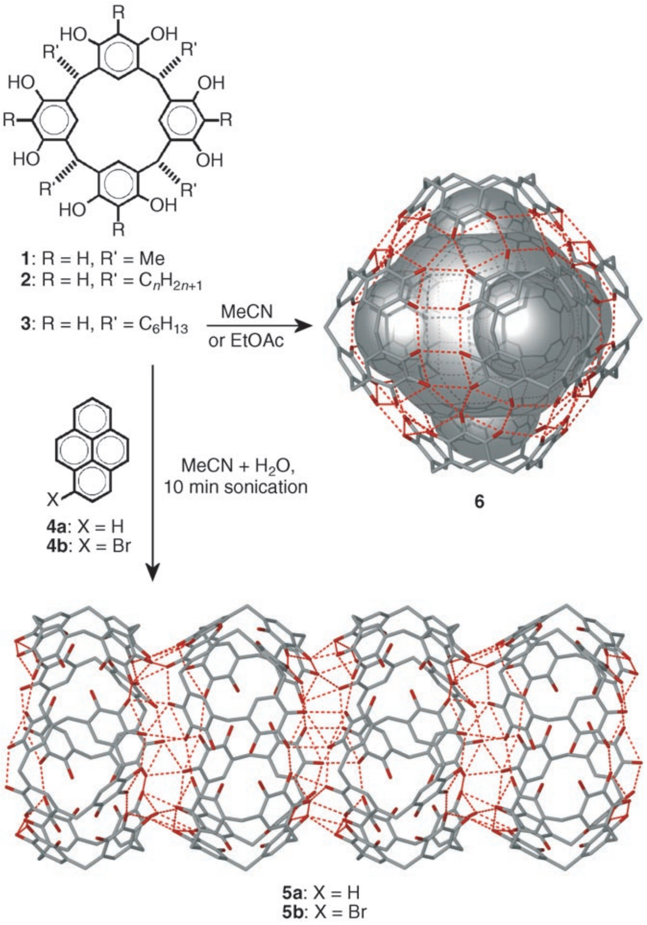

Figure 1. Conditions for the assembly of PgC6 (**3**) into organic nanospheroids (**6**) and nanotubes (**5a** or **5b**) through hydrogen-bonding interactions. For clarity, the *n*-hexyl side chains on the calixarene moieties are omitted.

running down the nanotube array. Examination of the footprint of the tube shows the dimensions between opposite calixarene centroids within each disc to be approximately 13.7 × 15.5 Å^2 (Figure 2). These dimensions are indicative of each disc adopting a slightly elliptical shape in the solid state. Opposing pairs of calixarenes within the corresponding PgC6 nanospheroid **6** grown from a solution of **3** in anhydrous acetonitrile have roughly equal cross-sphere separations and hence adopt a more spherical shape (see Figures 1 and 2).[23] Although there are slight differences in shape between the cross-sectional regions of each assembly, this is notably the third such example where spheres have been converted into nanotubes, hence suggesting not only that a general trend is developing but that any multicomponent spheroidal arrangement which contains large building blocks may exhibit similar behavior.[1–2,4–5]

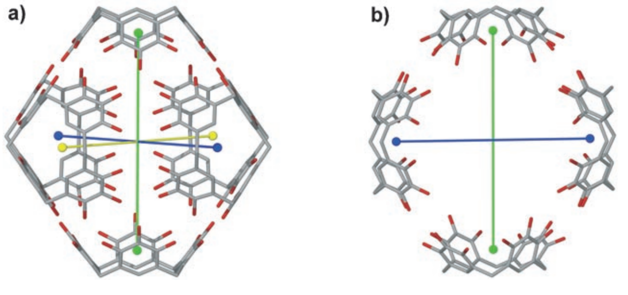

Figure 2. Distances between opposite calixarene pairs in spheroidal (a) and nanotubular (b) assemblies of PgC6. a) The three cross-sphere distances in **6** are roughly equal (green axis = 14.573; blue axis = 14.789; yellow axis = 14.884 Å), hence indicating a near-spheroidal shape. b) The dimensions of the cross-section of the nanotube **5** differ markedly (green axis = 15.486; blue axis = 13.679 Å) and show the calixarene tetramers adopt a slightly elliptical conformation. For clarity, the orientation of the sphere is skewed and the *n*-hexyl side chains on the calixarenes are omitted.

Upon examination, the calixarene discs that form the tube **5** through hydrogen-bonding interactions are found to shroud alternating solvent microenvironments of acetonitrile and water (Figure 3). These unprecedented organic nanotube solvent microenvironments are not only stabilized by a large number of intra- and interenvironment hydrogen-bonding interactions but they are also shielded from the exterior of the assembly (Figure 3b) and thus show the potential for simultaneous inclusion of different guest molecules within the walls of such nanotubular arrays. Unfortunately the presence of the PgC6 nanotubes **5** in the solution phase was ambiguous from FTIR studies.

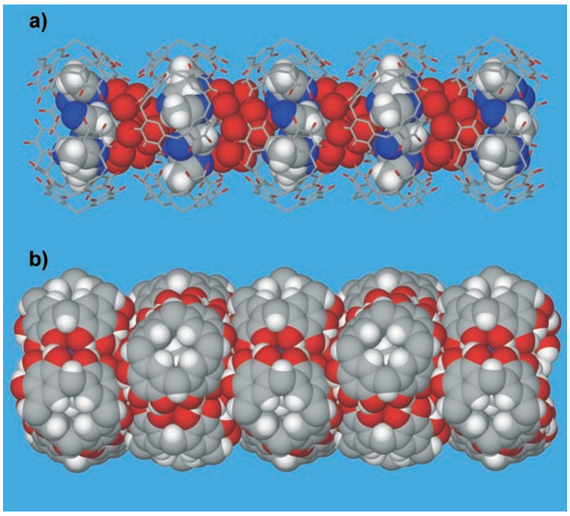

Figure 3. Partial (a) and full (b) space-filling views of the nanotubes **5** constructed from PgC6. a) The calixarene moities are shown in stick representation to emphasize the alternating acetonitrile and water microenvironments found in the tubular assembly. b) Full space-filling representation shows the calixarenes to shield the solvent microenvironments from the exterior of the nanotube through hydrogen-bonding interactions with the upper rim of the calixarene. For clarity, the *n*-hexyl side chains on the calixarene units are omitted. O red, N blue, C gray, H white.

When the alkyl chains on the lower rim of PgC6 are considered in the extended structure (Figure 4), it is immediately obvious that the exterior of the organic nanotubes interact through a large number of Van der Waals interactions between neighboring hydrophobic chains and intercalated pyrene molecules. The intercalation of hydrophobic pyrene

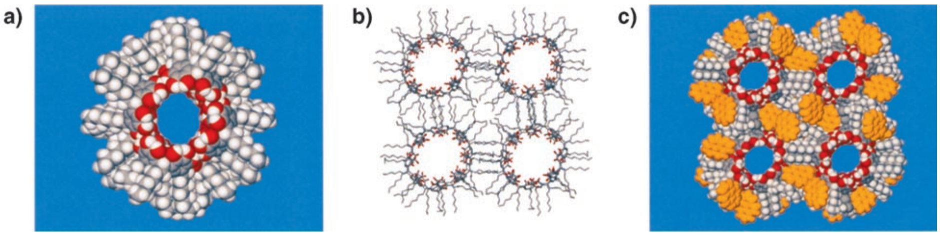

Figure 4. Different views of the extended structure of the organic nanotubes formed with PgC6 (**3**), pyrene (**4a**), acetonitrile, and water. a) View down the center of a single space-filled nanotube. b) Four neighboring nanotubes are shown in stick representation. c) View down four space-filling nanotubes showing the intercalated *exo*-tube pyrene molecules (orange). For clarity, solvent molecules are omitted in all parts and pyrene molecules are omitted in (a) and (b).

molecules within the outer layer of the tubes suggests that the presence of a suitable surfactant molecule, perhaps one that bears pyrene-functionalized tails, could lead to the isolation of such organic nanotubular arrays in the solution phase—a prospect we are currently exploring. Nanotubular arrays such as these could prove immensely useful for both industrial and academic communities alike if they were to be freestanding in the solution phase, be able to host or transport guest molecules, or act, for example, as regioselective catalysts or perhaps as microfilters in the solid state.

To conclude, we have demonstrated the formation of *C-n*-hexylpyrogallol[4]arene-based organic nanotubes **5** in the solid state that show some potential to maintain their structure in the solution phase. The nanotube cores are of similar dimensions to the nanospheroids **6** generated under different solvent conditions and are separated from typical calixarene-to-calixarene π-stacking interactions by the presence of hydrophobic tails that intercalate with one another and additional polyaromatic molecules (pyrene or bromopyrene). These organic nanotubes display alternating solvent microenvironments, thus demonstrating the hosting of disparate molecular material. In addition, we have noted the third such example where a sphere can be engineered into a related tube, thus indicating that any multicomponent spheroidal arrangement should be examined for similar behavior. Studies on the construction of alternative supramolecular arrangements with pyrogallol[4]arenes and the isolation of single and functional organic nanotubes in both the solid and solution states are in progress.

Received: August 25, 2005
Revised: September 13, 2005

Keywords: calixarenes · hydrogen bonds · nanostructures · self-assembly · supramolecular chemistry

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[20] In a typical experiment, a 1:1 mixture of PgC6 (**3**) and pyrene (**4a**) or 1-bromopyrene (**4b**) was dissolved in hot acetonitrile/water ($\approx 5{:}2$ by volume). The solution was sonicated for around 10 min and then left to stand overnight. Slow evaporation of the solvent resulted in the formation of large single crystals of **5a** or **5b**, respectively, that were suitable for X-ray diffraction studies. Data for both crystal structures were collected on a Bruker SMART 1000 CCD diffractometer. CCDC 282089 and 282090 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[21] Crystallographic data for pyrene-containing nanotube **5a** (CCDC 282089): $C_{145}H_{188.50}N_{4.50}O_{29.50}$, $M_r = 2444.33$, $0.35 \times 0.26 \times 0.22\ \text{mm}^3$, orthorhombic, $a = 35.446(7)$, $b = 36.868(7)$, $c = 22.124(4)$ Å, $V = 28913(10)$ Å^3, space group *Pccn*, $Z = 8$, $\rho_{\text{calcd}} = 1.123$, $\lambda(\text{Mo}_{\text{K}\alpha}) = 0.70930$ Å, $T = 173(2)$ K, 203224 reflections, 31906 unique (13021 observed, $R_{\text{int}} = 0.140$), $R_1 = 0.0941$, $\omega R_2 = 0.2913$ for 1507 parameters and two restraints.

[22] Crystallographic data for 1-bromopyrene-containing nanotube **5b** (CCDC 282090): $C_{145}H_{188.50}Br_2N_{4.50}O_{30.50}$, $M_r = 2642.32$, $0.40 \times 0.32 \times 0.26$ mm^3, orthorhombic, $a = 35.588(7)$, $b = 36.995(7)$, $c = 22.211(4)$ Å, $V = 29\,242(10)$ Å^3, space group $Pccn$, $Z = 8$, $\rho_{calcd} = 1.200$, $\lambda(Mo_{K\alpha}) = 0.70930$ Å, $T = 173(2)$ K, 139038 reflections, 32127 unique (15395 observed, $R_{int} = 0.0657$), $R_1 = 0.1176$, $\omega R_2 = 0.3222$ for 1627 parameters and one restraint. The structure showed significant disorder around the 1-bromopyrene molecules and this was modeled as satisfactorily as possible. The structure of the 1-bromopyrene derivative differs from that of the pyrene derivative by one water of crystallization. See Supporting Information for details of the asymmetric unit and figures of the extended structure.

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