Carbon Nanotubes

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Encapsulation and IR Probing of Cube-Shaped Octasilasesquioxane $H_8Si_8O_{12}$ in Carbon Nanotubes**

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Studying the encapsulation of molecules in carbon nanotubes is important because the physical properties of molecules and their chemical reactivity can be controlled by confining them in nanoscopic containers;[1] in turn, the functional properties of single-walled carbon nanotubes (SWNTs), such as the electronic band gap,[2] can be tuned by molecules nested inside. In general, molecules inserted into nanotubes can be divided into two groups. The first group includes small gas molecules whose interactions with the interior and exterior surfaces of nanotubes have been mainly investigated spectroscopically, notably by IR spectroscopy, to provide valuable information about the mechanisms and energy of molecule–nanotube interactions.[3] Nevertheless, it is often difficult to distinguish conclusively between endohedral and exohedral adsorption of such small molecules. The other class of molecules are relatively large, carbon-rich molecular polyhedra, such as fullerenes[4a] and *ortho*-carboranes,[4b] or planar organic compounds, such as derivatives of perylene,[5] for which the use of IR spectroscopy is hindered by the overlap of their absorption bands with those of nanotubes, and whose presence inside nanotubes is usually unambiguously demonstrated by transmission electron microscopy (TEM).

Oligosilasesquioxanes of general formula $(HSiO_{3/2})_{2n}$ (n = 2, 3, 4,…)[6,7] have vibrational spectra whose distinct features do not overlap with absorption bands of nanotubes,[7–9] which, in principle, should enable IR, Raman, and neutron-scattering spectroscopies to reveal the mechanism of their interaction with nanotubes. $H_8Si_8O_{12}$, for example, is a cube-shaped molecule with an H atom pointing outwards from each corner of the cube (Figure 1). Since the Si–H bonds are outermost in $H_8Si_8O_{12}$, their stretching vibrations are highly sensitive to the environment around the molecule and could potentially be used to probe the interactions between $H_8Si_8O_{12}$ and nanotubes.

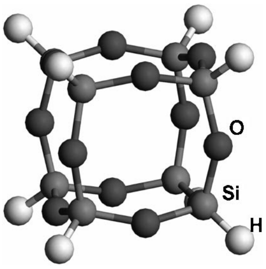

Figure 1. Structural diagram of $H_8Si_8O_{12}$. Selected geometrical parameters:[8] r(Si–H) = 0.148 nm, r(Si–O) = 0.162 nm, α(O-Si-H) = 109.5°, β(O-Si-O) = 109.5°, γ(Si-O-Si) = 148.4°.

Like most other molecular species, $H_8Si_8O_{12}$ is expected to interact with nanotubes through low-directional nonspecific van der Waals forces[10] and, depending on the nanotube diameter, it can experience a significant pressure inside nanotubes,[11] so that the properties of the encapsulated molecules are expected to be altered from those in the bulk crystal or solution phase. The diagonal distance of 0.66 nm between H atoms on the same face of the cube is slightly shorter than the diameter of C_{60} molecules (0.7 nm), which were previously inserted into nanotubes. As the van der Waals radius of an sp^2 carbon atom in the nanotube walls and an H atom in $H_8Si_8O_{12}$ are about 0.15 and 0.12 nm, respectively,[12] it is expected that the smallest tube diameter capable of being filled with octasilasesquioxane would be around 1.2 nm ($= 0.66 + 2 \times 0.15 + 2 \times 0.12$ nm). Because hydrogen atoms of $H_8Si_8O_{12}$ come into direct contact with the nanotube surface when the molecule is lodged inside, the vibrational frequency of the Si–H bonds might be suitable for spectroscopic probing of the interiors of nanotubes to characterize their properties as nanoscopic molecular containers. We have investigated this possibility for SWNTs and multiwalled carbon nanotubes (MWNTs) of different diameters.

We found that $H_8Si_8O_{12}$ can be efficiently inserted into SWNTs with diameters of 1.4–1.5 nm (SWNT-1) and MWNTs with internal diameters of 1.0–3.0 nm and an average diameter of 1.85 nm (MWNT-1) in the gas phase to yield nanotubes filled with $H_8Si_8O_{12}$ molecules, as evidenced by high-resolution TEM (HRTEM) imaging (Figure 2). This observation is in agreement with the fact that the average diameters of SWNT-1 and MWNT-1 used in these experiments are both larger than the estimated minimum diameter of 1.2 nm required for insertion of $H_8Si_8O_{12}$. Unlike in the case of fullerenes, no ordered packing patterns were observed for $H_8Si_8O_{12}$ molecules inside the nanotubes by HRTEM. One reason for this could be related to different orientations of $H_8Si_8O_{12}$ molecules in a nanotube (Figure 2 d), which result in different projected shapes of $H_8Si_8O_{12}$ on the viewing plain in TEM and complicate the contrast in electron micrographs.

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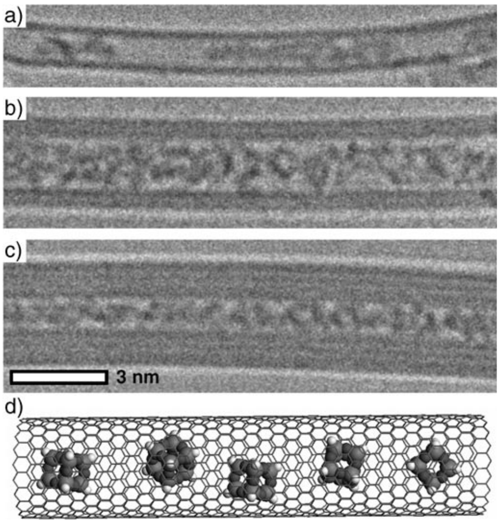

Figure 2. HRTEM images of a) $H_8Si_8O_{12}$@SWNT-1, b) $H_8Si_8O_{12}$@MWNT-1, and c) $H_8Si_8O_{12}$@MWNT-1 with narrow internal diameter (ca. 1.2 nm); d) schematic diagram of $H_8Si_8O_{12}$ encapsulated in a SWNT.

Using supercritical CO_2 ($scCO_2$) as solvent for transporting molecules into carbon nanotubes, a method successfully utilized for insertion of fullerenes,[13] resulted in only partial filling with $H_8Si_8O_{12}$. This can probably be explained by the high affinity of silicon compounds for $scCO_2$,[14] which results in preferential solvation of $H_8Si_8O_{12}$ by CO_2 and thus reduced insertion into the SWNTs. The energy of the interaction of octasilasesquioxanes with the nanotube interior may be lower than that for C_{60} (ca. 3 eV),[15] and this may further reduce the efficiency of filling in supercritical fluids. The filling factor for MWNT-1 in $scCO_2$ appears to be somewhat higher than for SWNT-1 under the same conditions but lower than in the gas phase.

The most striking effect of encapsulation in carbon nanotubes on the vibrational spectra of $H_8Si_8O_{12}$ is a red shift of the ν(Si–H) band, by about $-15\ cm^{-1}$ for SWNT-1 and about $-19\ cm^{-1}$ for MWNT-1 (Figure 3 and Table 1). A shift of opposite sign ($+17\ cm^{-1}$) is observed for $H_8Si_8O_{12}$ in the crystal (Table 1 and Supporting Information), that is, the molecules in $H_8Si_8O_{12}$@SWNT-1 and $H_8Si_8O_{12}$@MWNT-1 are not in a crystal-like state. Inside SWNT-1 with diameters of 1.3–1.5 nm used in our experiments each octasilasesquioxane molecule has only two nearest neighbors because of the geometrical constraint imposed by the nanotube (Figure 2b). In such an arrangement most or all of the H atoms of $H_8Si_8O_{12}$ will point towards the nanotube sidewalls (Figures 4b and c), so that $\tilde{\nu}$(Si–H) will be directly affected by any interaction between $H_8Si_8O_{12}$ and the nanotube interior. The most likely explanation for the shift of $\tilde{\nu}$(Si–H) is elongation of the Si–H bonds as a result of dispersion forces acting between $H_8Si_8O_{12}$ and the nanotube. A similar effect was reported for various small molecules such as $(NO)_2$ and CF_4 adsorbed in nanotubes from the gas phase.[16,17]

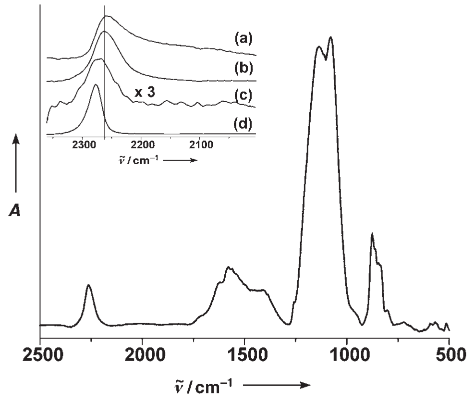

Figure 3. A typical FTIR spectrum of octasilasesquioxane in carbon nanotubes. Inset: ν(Si–H) band for a) $H_8Si_8O_{12}$@MWNT-1, b) $H_8Si_8O_{12}$@SWNT-1, and c) $H_8Si_8O_{12}$@SWNT-2, as compared to the ν(Si–H) band of free octasilasesquioxane dissolved in CCl_4 (d).

Table 1: Characteristics of the ν(Si–H) band for octasilasesquioxane in various environments.

Sample	Nanotube int. diam. [nm]	Peak position [cm^{-1}]	Shift [cm^{-1}][a]	Peak width [cm^{-1}][b]
$H_8Si_8O_{12}$ solution (CCl_4)	–	2277	–	25
$H_8Si_8O_{12}$ solid (KBr)	–	2294, 2300[c]	+17	20
$H_8Si_8O_{12}$@SWNT-1	1.3–1.5	2262	−15	50
$H_8Si_8O_{12}$@MWNT-1	1.0–3.0	2258	−19	>50[d]
$H_8Si_8O_{12}$@SWNT-2	0.8–1.2	2271	−6	40
$H_8Si_8O_{12}$@MWNT-2	5–8	no peak	–	–

[a] Shifts were calculated from the peak maxima relative to $\tilde{\nu}$(Si–H) in CCl_4 solution[8] (uncertainty in peak position $< \pm 2\ cm^{-1}$). [b] Full width at half maximum obtained from Lorentzian curve fit. [c] In CsI pellet three bands were observed: 2274, 2293, 2300 cm^{-1}.[9] [d] The ν(Si–H) band is unsymmetrical.

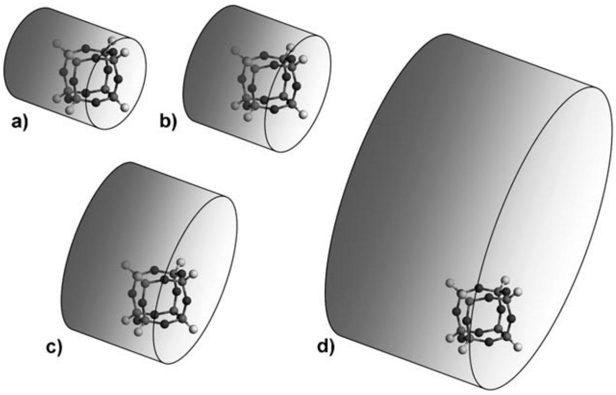

Figure 4. Scaled representation of the average internal diameters of a) SWNT-2, b) SWNT-1, c) MWNT-1, and d) MWNT-2 in relation to the size of $H_8Si_8O_{12}$.

A twofold broadening of the ν(Si–H) band in nanotubes as compared to solution (Figure 3, Table 1) can be explained by the high degree of disorder inside nanotubes, which is also evidenced by HRTEM imaging (Figure 2). Such disorder creates a distribution of different local environments for $H_8Si_8O_{12}$ in nanotubes, reflected in the shape of the ν(Si–H) band. The distribution of different orientations of $H_8Si_8O_{12}$

inside MWNT-1 and therefore the width of the band are expected to be sensitive to the internal diameters of nanotubes. We found that the broadening of the ν(Si–H) band for $H_8Si_8O_{12}$@MWNT-1 (Figure 3, spectrum (a) in the inset) is substantially greater than for $H_8Si_8O_{12}$@SWNT-1 (spectrum (b) in the inset). This can be related to the broader spread of internal diameters of MWNT-1 ($d_{NT} = 1.0–3.0$ nm) than of SWNT-1 ($d_{NT} = 1.3–1.5$ nm).

We also attempted insertion of $H_8Si_8O_{12}$ into carbon nanotubes of average diameter smaller than the size of the molecule (ca. 1.0 nm). The filling rate for SWNTs with diameters of 0.8–1.2 nm (SWNT-2), qualitatively estimated from extensive HRTEM imaging, appeared to be lower than for SWNT-1 or MWNT-1, and this resulted in a low intensity of the ν(Si–H) band in the IR spectrum of $H_8Si_8O_{12}$@SWNT-2 (Figure 3, spectrum (c) in the inset). The red shift of the ν(Si–H) peak is only $-6\,cm^{-1}$ in SWNT-2, much smaller than in wider SWNT-1 or MWNT-1. Such a small shift indicates that, in addition to van der Waals dispersive forces, the molecules in narrower nanotubes (Figure 4 a) may experience greater compression than in wider nanotubes. The compression effect was previously reported for fullerenes encapsulated in carbon nanotubes of small diameters,[11] and since van der Waals forces are also responsible for the $H_8Si_8O_{12}$–nanotube interaction, a similar effect can be expected for $H_8Si_8O_{12}$ in nanotubes. Such a compression would shorten the Si–H bonds and effectively compensate for their elongation caused by the dispersion interactions and thus suppress the observable red shift of the ν(Si–H) band. The width of the ν(Si–H) band of $H_8Si_8O_{12}$@SWNT-2 is about $40\,cm^{-1}$.

We also explored encapsulation of $H_8Si_8O_{12}$ in carbon nanotubes with diameters greatly exceeding the dimensions of the molecules, but in this case no ν(Si–H) peak was observed in the IR spectra. Open-ended MWNT-2 with internal diameters in the range between 5 and 8 nm was filled with octasilasesquioxane under standard conditions in the gas phase. An $H_8Si_8O_{12}$@MWNT-2 sample was washed with hexane to remove unencapsulated octasilasesquioxane from the nanotube surfaces (in the same way as for all other samples), and this caused complete loss of the ν(Si–H) peak in the IR spectrum, attributed to removal of the molecules from the interior of MWNT-2 by the wash solvent. As the internal diameters of MWNT-2 are substantially larger than the size of $H_8Si_8O_{12}$ (Figure 4 d), fewer nanotube carbon atoms are involved in van der Waals interactions per enclosed molecule, and not all sides of the octasilasesquioxane molecules interact with the nanotube, which reduces the efficiency of the nanotube–molecule interactions. Because of the loose geometrical fit of the molecules and MWNT-2, the solvent penetrates into the nanotubes and dissolves and removes $H_8Si_8O_{12}$ from the nanotubes during the washing procedure. This also indicates that in the case of wide-nanotube MWNT-2 it is energetically favorable for $H_8Si_8O_{12}$ to be dissolved in an organic solvent rather than to be encapsulated inside the nanotube.

We have demonstrated that the effectiveness of interactions of $H_8Si_8O_{12}$ with carbon nanotubes depends critically on the internal diameter of the nanotubes. Nanotubes with diameters slightly exceeding the size of the molecules form efficient van der Waals interactions with $H_8Si_8O_{12}$, manifested in a red shift of 15–19 cm^{-1} of the Si–H vibration. Narrow nanotubes with diameters close to the size of the molecules exert pressure on the encapsulated molecules and reduce the shift of the ν(Si–H) band, whereas nanotubes with diameters substantially exceeding the size of the molecules interact weakly with $H_8Si_8O_{12}$ and are unable to retain it. We believe that encapsulation of octasilasesquioxane may be used to quantify the interactions of nanotubes with molecules and to distinguish nanotubes of different internal diameters by using $H_8Si_8O_{12}$ as a spectroscopic probe, by applying the principles outlined in this communication and further quantitative IR analyses which we are planning to carry out.

Experimental Section

$H_8Si_8O_{12}$ was synthesized and purified by an established method.[18] Four types of carbon nanotubes were used for the experiments: SWNT-1 produced by arc-discharge (Aldrich) with diameters of 1.3–1.5 nm after purification,[19] MWNT-1 (Nanocyl) with a distribution of internal diameters of 1.0–3.0 nm, SWNT-2 produced by HiPCO (Carbon Nanotechnologies) with diameters of 0.8–1.2 nm, and MWNT-2 (Aldrich) with internal diameters of 5–8 nm. Prior to filling with $H_8Si_8O_{12}$, SWNTs were oxidized in air at 400 °C for 30 min to open the nanotube caps and partly remove amorphous carbon from their surfaces. MWNTs were treated with 5 M HNO_3 prior to heating in air to ensure that the nanotube ends were open. The mixtures of open-ended nanotubes and $H_8Si_8O_{12}$ were placed in a quartz tube, sealed under a vacuum of 10^{-3} Torr and heated at 175–177 °C for two days[20] or treated in supercritical $scCO_2$ at 50 °C under 15 MPa by using a pressure-cycling filling technique reported previously by us.[13] Following the filling processes, each sample was sonicated in hexane followed by filtration and washing with more hexane to remove unencapsulated $H_8Si_8O_{12}$. Prior to spectroscopic characterizations all samples were analyzed by thermogravimetric analysis (TGA), whereby the absence of weight loss at 126 °C, characteristic of desorption of $H_8Si_8O_{12}$ from the surface of nanotubes, confirmed that $H_8Si_8O_{12}$ is encapsulated in the nanotubes (see the Supporting Information). Nanotube diameter distributions were measured by HRTEM imaging.

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