

# Molecules in Carbon Nanotubes

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Received June 2, 2005

## ABSTRACT

This Account focuses on structural and dynamic behavior of molecules encapsulated in carbon nanotubes. The impact of the confinement on the molecular packing, orientation, translation, rotation, and reactivity is demonstrated for a range of fullerene and nonfullerene molecules. These phenomena are described and analyzed using the current understanding of molecule–nanotube and intermolecular interactions.

## Introduction

Carbon nanotubes (NTs) are attracting a great deal of attention as structures possessing remarkable physical properties such as high mechanical strength, coherent electron transport, and excellent thermal properties.<sup>1</sup> Due to their unique properties, NTs are being explored for many future commercial and industrial products in virtually all areas of science. From a chemist's perspective, one of the most fascinating properties of nanotubes is their ability to encapsulate molecules and confine them to form quasi-1D arrays. Many reports on molecule-filled NTs concentrate on the physical properties of the nanotubes and their response to the presence of the absorbed molecules, which are viewed as dopants controlling nanotube properties such as conductance<sup>2</sup> or electronic band gap.<sup>3</sup> The central aim of this Account is to sum up known information about the *structural and dynamic behavior*

of molecules encapsulated in carbon nanotubes. The examples presented here compare the impact of confinement on the molecules with their unconfined state (solid or solution) to illustrate the potential applications of carbon nanotubes in chemistry. Because ionic inorganic structures inside NTs have been well reviewed,<sup>4</sup> this Account considers only molecular systems in carbon nanotubes.

## C<sub>60</sub> in Carbon Nanotubes

The first molecule ever reported inside carbon nanotubes was the Buckminster fullerene C<sub>60</sub>.<sup>5</sup> The insertion of C<sub>60</sub>, formed together with nanotubes by a pulsed laser vaporization method, occurred accidentally during postsynthesis processing of the nanotubes and was confirmed unambiguously by high-resolution transmission electron microscopy (HRTEM) in 1998, marking the beginning of the new class of molecular self-assembled nanomaterials. Nanotubes filled with fullerenes were named “peapods” because of their similar appearance, and fullerenes have remained the favorite type of molecule to insert into nanotubes, as evidenced by the vast majority of studies dedicated to peapods as compared to nanotubes filled other types of molecules.

Fullerenes are the choice of guest for NTs for more than historical reasons, as both fullerenes and nanotubes are structurally related graphitic materials made by similar processes. Highly effective van der Waals forces and the perfect geometrical match of the shape of a fullerene and the interior of a nanotube provide a highly efficient interaction that can be as high as 3 eV per C<sub>60</sub>, i.e., 50% higher than the cohesive energy of fcc fullerene crystal.<sup>6</sup> This indicates that the encapsulation of C<sub>60</sub> in single-walled nanotubes (SWNTs) is a spontaneous and irreversible process, provided that the nanotube diameter is about 0.6 nm wider than the fullerene diameter to allow for the thickness of the  $\pi$ -orbitals of the graphitic structures (Figure 1). In addition, fullerenes provide good contrast and are stable under the e-beam of a TEM, which facilitates their imaging and analysis.

## Intermolecular Spacing

As a result of encapsulation in nanotubes, intermolecular interactions are expected to be altered substantially compared with the bulk crystal or the solution phase. For example, the energy gain of a fullerene entering a nanotube is manifested as a 0.5 nN force on each C<sub>60</sub> driving the fullerene into a (10,10) nanotube.<sup>7</sup> Based on this observation, it has also been suggested that an effective pressure of about 1 GPa exists inside a fullerene-filled nanotube, which should significantly shorten the intermolecular spacing as compared to the crystal.<sup>8</sup> Secondary effects related to the orbital interactions between nano-

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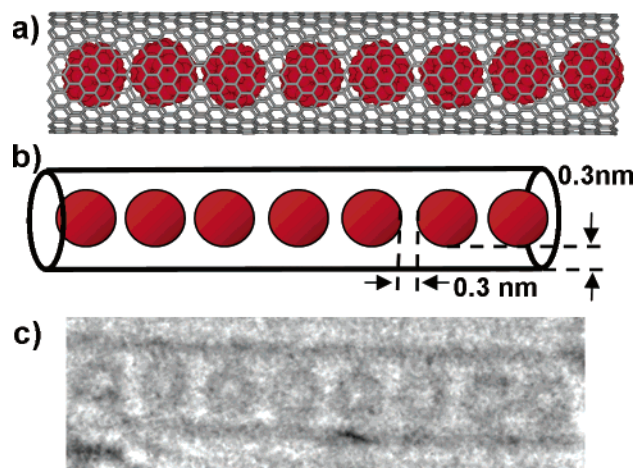
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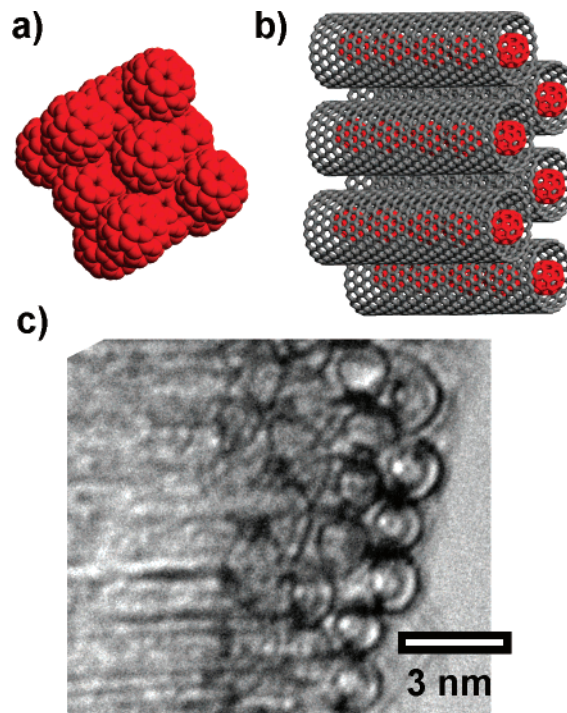
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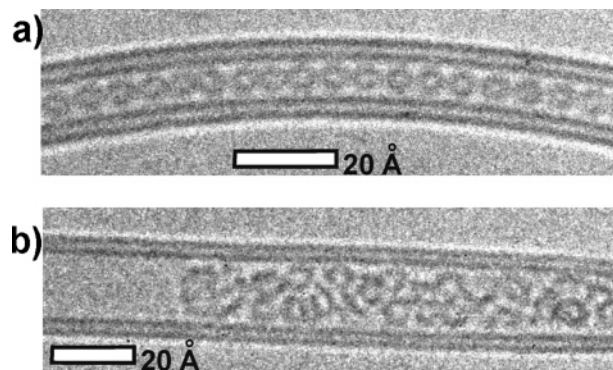
**FIGURE 1.** Structural diagram (a), schematic representation (b), and HRTEM micrograph (c) of C<sub>60</sub>@SWNT.

tubes and the guest molecules, together with van der Waals forces, can also perturb the state of the molecules.<sup>9</sup>

The intermolecular separation can be used to probe the interactions between the molecules. The distance between molecules can be measured by conventional direct space HRTEM imaging: the micrographs essentially represent 2D projections of the peapod structures onto the photographic plane where each C<sub>60</sub> fullerene molecule can be seen as a circle encased between the nanotube walls appearing as two parallel lines (Figure 1b,c). The intermolecular separation for C<sub>60</sub> is on the order of 1 nm, which is close to the interfullerene separation of 1.004 nm in a fcc C<sub>60</sub> crystal.<sup>10</sup> The similar interfullerene spacing is a good experimental indication that the nature of the interfullerene and the fullerene–nanotube interactions is van der Waals forces, similar to those in fullerene crystals (Figure 2a) or between sheets of graphite. It was also found that a simple Lennard-Jones potential<sup>11</sup> could describe peapod geometry quantitatively, giving further evidence that the nature of the interaction is dominated by van der Waals' forces. More accurate methods than HRTEM for determining intermolecular spacing provide valuable information about subtle differences between behaviors of the molecules inside nanotubes and in the bulk crystal. Because of its 3D periodicity, the structure of a macroscopic fullerene crystal can be determined by single-crystal X-ray diffraction with an accuracy of  $\pm 0.001$  nm.<sup>10</sup> Single-walled carbon nanotubes tend to form large bundles with tens or hundreds of nanotubes aligned parallel to each other similar to the logs in a raft (Figure 2b,c). The electron beam in a TEM can be condensed to dimensions comparable to that of the bundle, and thus an e-beam diffraction pattern can be taken, revealing weak diffraction features corresponding to periodically spaced C<sub>60</sub>.<sup>12</sup> From the initial diffraction measurements, it was concluded that the intermolecular spacing tends to be 3% shorter in nanotubes than in bulk crystals,<sup>13</sup> which would be consistent with the compression of fullerenes inside nanotube as a result of van der Waals forces.<sup>8</sup> Similar measurements were subsequently made on improved samples of C<sub>60</sub>@SWNT peapods using an internal standard for analyz-



**FIGURE 2.** Fragment of the crystal structure of C<sub>60</sub> (a) and structural diagram (b) and HRTEM micrograph (c) of a bundle of C<sub>60</sub>@SWNTs.

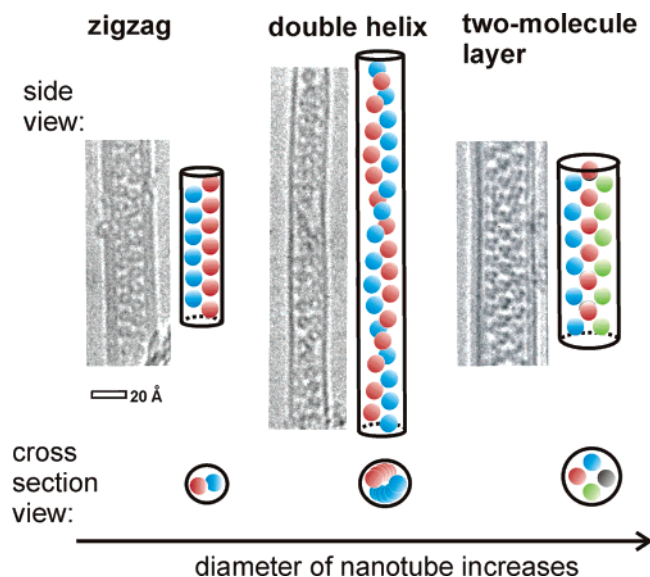


**FIGURE 3.** HRTEM micrographs of C<sub>60</sub>-filled double-walled nanotubes with internal diameters of 1.1 nm (a) and 2.2 nm (b).

ing the diffractograms; these demonstrated that in fact there is no measurable difference between C<sub>60</sub>–C<sub>60</sub> distances in nanotubes or in the bulk crystal.<sup>13</sup>

The first indication that the structural behavior of C<sub>60</sub> fullerenes confined in carbon nanotubes can be qualitatively different from the bulk came from studies of C<sub>60</sub> in double-walled carbon nanotubes (DWNTs).<sup>14,15</sup> Fullerenes formed regular peapod structures in DWNTs with narrow internal diameters similar to those in SWNTs (Figure 3a); in wider DWNTs, fullerenes were found to be disordered (Figure 3b). Theoretical calculations predict that the ordering of molecules in nanotubes depends on temperature, so C<sub>60</sub>@NTs, which form a highly ordered structure at low temperature, become disordered as higher temperature. The temperature of the order–disorder transition in turn depends on the filling factor and the diameter of the nanotube: in a partially filled 2 nm wide (15,15)-nanotube, an ordered zigzag phase of C<sub>60</sub> undergoes melting into a disordered one at 75 K.<sup>16</sup> Unlike melting of





**FIGURE 4.** Dependence of the packing arrangement of  $C_{60}$  inside NTs on nanotubes internal diameters.

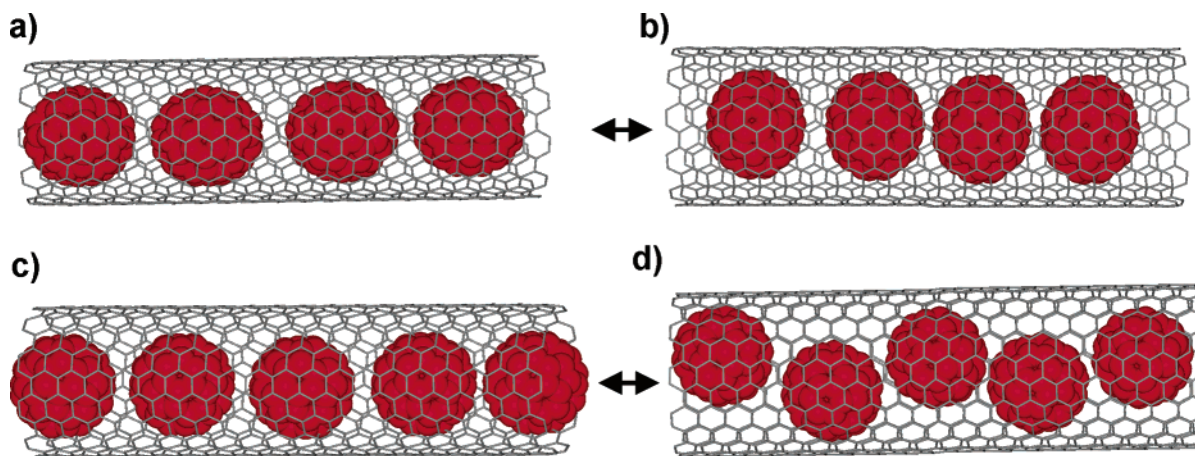
solids in the bulk, the order–disorder transition can be controlled by the nanotube filling ratio, and hence heating of partially filled DWNTs with an excess of  $C_{60}$  in the gas phase enables the observation of the ordered phases at room temperature (Figure 4). The type of the packing arrangement of  $C_{60}$  appears to depend on the internal diameter of the nanotubes, resembling the packing of hard macroscopic spheres inside hard cylinders.<sup>17</sup> Ten possible arrangements for  $C_{60}$  inside nanotubes are possible,<sup>18</sup> none of which can exist in the bulk. This phenomenon is an observable manifestation of the confinement effect inside nanotubes. The zigzag phase formed in nanotubes with internal diameter 1.45–2.16 nm can be imaged in HRTEM, but more complex structures such as the two-molecule layer and the double helix are more difficult to visualize since fullerene projections overlap (Figure 4). The double helix appears to be significantly less abundant than the zigzag phase as it can exist only for a very narrow 0.07 nm range of nanotubes ( $d = 2.16$ – $2.23$  nm).

## Molecular Orientation

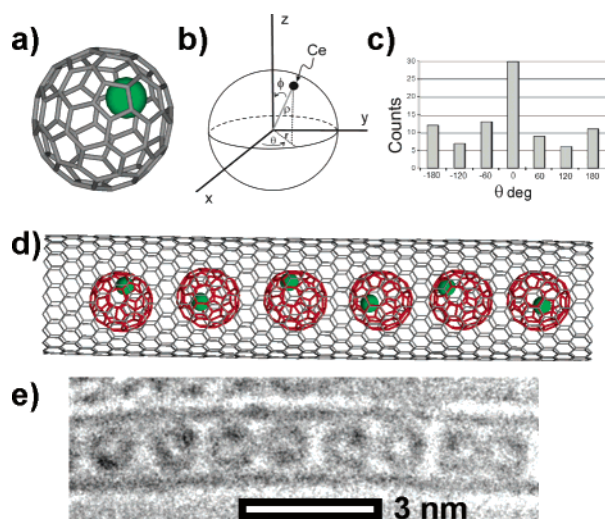
The internal diameter of the nanotubes is important not only for the molecular packing of encapsulated molecules, but also for their orientation. X-ray and electron diffraction studies carried out for nanotube bundles filled with  $C_{70}$ , a fullerene of similar size to  $C_{60}$  but with elongated “rugby ball” shape, revealed two sets of reflections corresponding to two different intermolecular spacings, 1.00 and 1.10 nm,<sup>12</sup> attributed to distinct transverse and longitudinal orientations of the ellipsoidal  $C_{70}$  in nanotubes (Figure 5a,b). In a  $C_{70}$  crystal at room temperature, the rotation around the long molecular axis is frozen,<sup>19</sup> but the alignment of  $C_{70}$  inside SWNTs may have a different origin. DFT calculations performed for  $C_{70}$ @SWNTs structures with diameters 1.49 and 1.36 nm, combined with experimental HRTEM/Raman study for the same diameters, shed light on the alignment mechanism.<sup>20</sup> In narrower 1.36

nm nanotubes, the elongated fullerene molecules adopt exclusively a longitudinal orientation to minimize the repulsive component of van der Waals interactions with the interior of nanotubes (Figure 5a); in wider 1.49 nm nanotubes, the molecules are oriented in a transverse fashion to maximize the attractive component of van der Waals interactions (Figure 5b). The modeling also predicted the existence of intermediate orientations of  $C_{70}$  in SWNTs with diameters between 1.36 and 1.49 nm, thus indicating that the molecular orientation depends continuously on the nanotube diameter, and suggesting a mechanism for controlling molecular arrays. The difference in energy between the longitudinal and the transverse orientations in 1.36 nm nanotubes is 0.6 eV, and that in 1.49 nm nanotubes is 0.02 eV, whereas the difference between the transverse and the longitudinal orientations of isolated chains of  $C_{70}$  fullerenes with van der Waals intermolecular separations at the chain repeat distances was found to be less than 0.002 eV. Thus, the molecular orientations in these systems are dictated by fullerene–nanotube interactions rather than by fullerene–fullerene interactions. For  $C_{60}$ , such a difference in nanotube diameters would have a different consequence: since 1.45 nm is a threshold nanotube diameter below which  $C_{60}$  molecules form a linear array and above which they form a zigzag phase; the difference between 1.36 and 1.49 nm nanotubes would result in a phase transition of  $C_{60}$  (Figure 5c,d) rather the change of orientation, as observed for  $C_{70}$ . Again, the dominant interaction for such a phase transition in  $C_{60}$  would be the fullerene–nanotube interaction,<sup>16,18</sup> though this shifts toward  $C_{60}$ – $C_{60}$  interaction energy dominating as the coordination number of each fullerene and the diameter of the nanotube increase.

So far we have considered van der Waals forces as major interactions defining the geometry of molecular systems of fullerenes  $C_{60}$  and  $C_{70}$ . Endohedral metallofullerenes containing one or more metal atoms inside the carbon cage have an asymmetric charge distribution as a result of interaction of the incarcerated metal atom with the cage (Figure 6a). These molecules possess electric dipole moments that influence their behavior inside nanotubes. The effect of the dipolar interactions on molecular orientations in carbon nanotubes can be observed for  $Ce@C_{82}$  molecules, whose orientations can be visualized and analyzed by using HRTEM through the high single-atom contrast of Ce (Figure 6). The angle  $\theta$ , a projection of the dihedral angle between the direction of the molecular dipole and the axis of the nanotube, can be measured from the micrographs, and the  $\theta$  distribution for many  $Ce@C_{82}$  fullerenes shows that the molecules have a tendency to align their dipolar moments along the nanotube axis and to maximize the electrostatic interactions between neighboring molecules. Such alignment is not observed in the bulk crystal or solution of  $Ce@C_{82}$ , where the molecules are freely rotating at room temperature, and depends on the quasi-1D confinement of the polar molecules in the nanotube.<sup>21</sup> The metallofullerene orientation is likely to be driven by electrostatic dipole forces and is dominated by nearest neighbor fullerene–



**FIGURE 5.** Structural diagrams of a longitudinal orientation of  $C_{70}$  in (10,10)NT ( $d = 1.36$  nm) (a), a transverse orientation of  $C_{70}$  in (11,11)NT ( $d = 1.49$  nm) (b), a straight chain packing of  $C_{60}$  in (10,10)NT ( $d = 1.36$  nm) (c), and a zigzag packing of  $C_{60}$  in (11,11)NT ( $d = 1.49$  nm) (d).



**FIGURE 6.** Structural (a) and schematic (b) diagrams of  $Ce@C_{82}$ , distribution of angle  $\theta$  in peapods (c), and structural diagram (d) and HRTEM micrograph (e) of  $(Ce@C_{82})@SWNT$ .

fullerene interactions, though some contribution of fullerene–SWNT interactions in the molecular alignment is also possible.

## Molecular Motion

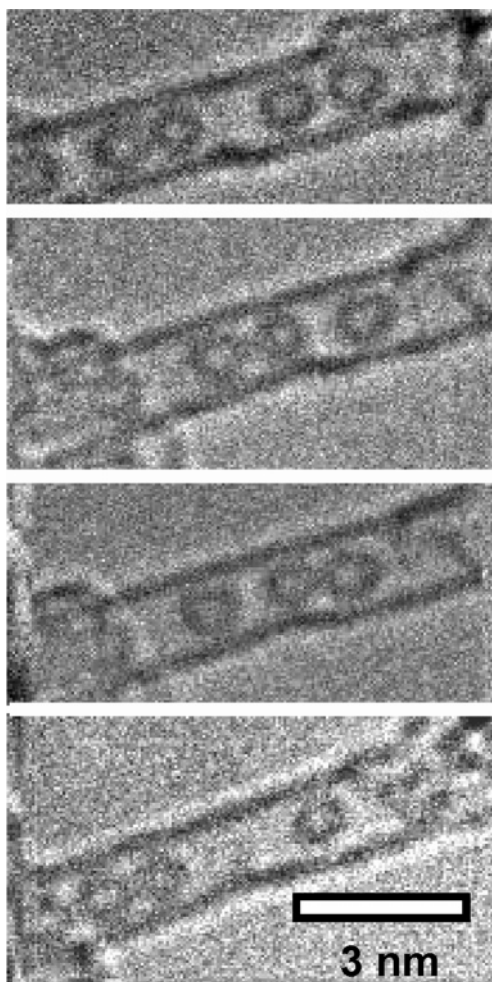
The nanotube–fullerene interactions are strong but, because of the uniform surface inside the nanotube, the molecules can move from one position to another with only weak barriers between different registrations.<sup>22</sup> Indeed the rotation of  $Ce@C_{82}$  can be seen at room temperature (albeit under the influence of the electron beam) as the dark spot on HRTEM micrographs changes its position every few seconds.<sup>23</sup> The rotation appears as a series of abrupt rotational jumps each followed by several seconds of “resting” time, indicating the presence of the energetic barriers for the rotation on the order of  $\sim 0.2$  eV. Such rotational barriers are almost negligible at room temperature in the bulk crystal of  $Ce@C_{82}$ ;<sup>23</sup> their origin inside nanotubes can be attributed to the decrease in the coordination number of  $Ce@C_{82}$  from 12 in the bulk crystal

(12 nearest neighbors around each molecule) to 2 within the peapod structure, which in turn increases the directionality and hence the efficiency of the fullerene–fullerene interaction.

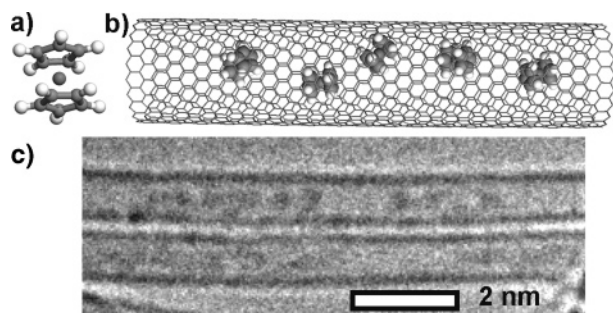
The confinement in SWNTs affects the tumbling motion of endohedral atoms inside fullerene cages of  $La_2@C_{80}$ .<sup>24</sup> When the molecule is in solution, the pair of La-atoms rotates freely and uniformly. However, when  $La_2@C_{80}$  is encapsulated in a 1.4 nm SWNT, the endohedral La-atoms are positioned closer to sides of the fullerene cage and their tumbling becomes discontinuous; the observed ratcheting is attributed to the energetic barriers for tumbling induced by the interactions between the molecules and the nanotube.

Molecular translation can also occur inside nanotubes, in a way that is scarcely possible in bulk fullerene crystals, though surface diffusion is possible. Translation can be observed in partially filled SWNTs where the gaps between the fullerenes exceed the molecular dimensions. A weak attraction between molecules can bring them together until they reach the optimum van der Waals separation. The molecules move from one position to another rather abruptly with several second intervals between the jumps (Figure 7). HRTEM analysis provides valuable information by allowing observation inside NTs, but effects of the electron beam on the molecules should be taken into consideration when interpreting the micrographs. Ionization and the heating effects of the e-beam on carbon nanotubes are probably negligible since carbon nanotubes are superb heat and electrical conductors, but ballistic knock-on collisions may be important for carbon nanomaterials.<sup>25</sup> The transferable energy for knock-on collisions, strongly dependent on the accelerating voltage of the microscope, is significantly minimized at 100 kV compared with higher accelerating voltages. The micrographs in Figures 1–7 were taken at 100 kV, using a small electron current density to minimize the effect of the e-beam, but even under these conditions, it would be difficult to estimate how much the molecules are influenced by collisions with electrons.





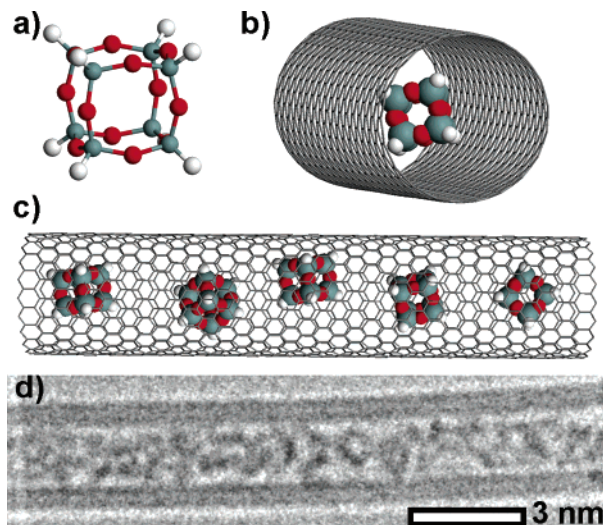
**FIGURE 7.** Time series of micrographs of a sparsely filled nanotube showing translation of fullerenes.



**FIGURE 8.** Structural diagrams of cobaltocene  $\text{CoCp}_2$  (a) and  $\text{CoCp}_2$ @SWNT (b) and HRTEM micrograph (c) showing two nanotubes filled with  $\text{CoCp}_2$ .

## Interactions of Non-Fullerene Molecules with Nanotubes

Metallocenes, organometallic molecules of a cylindrical shape, are one of the few non-fullerene type molecules within the scope of this Account whose properties have been studied inside NTs (Figure 8). HRTEM imaging of metallocenes is difficult because they are significantly affected by the e-beam, causing displacement and possibly decomposition inside nanotubes.<sup>26,27</sup> The energy of the interaction of  $\text{CoCp}_2$ , a cylindrical molecule with a Co-



**FIGURE 9.** Structural diagram of octasiloxane  $\text{Si}_8\text{H}_8\text{O}_{12}$  (a) and  $\text{Si}_8\text{H}_8\text{O}_{12}$ @SWNT (b,c) and HRTEM micrograph (d) of double-walled nanotube filled with octasiloxane.

atom sandwiched between two cyclopentadienyl rings, with a carbon NT was predicted to be only about 0.1 eV,<sup>28</sup> which is significantly lower than the fullerene–nanotube interaction. However, the nature of the  $\text{CoCp}_2$ –NT interaction appears to be more complex than pure van der Waals forces.  $\text{CoCp}_2$  and  $\text{Co}(\text{CpEt})_2$  in SWNTs were probed by UV–vis absorption spectroscopy revealing that the oxidation state of Co is changed from +2 to +3 upon insertion of these metallocenes into SWNTs.<sup>27</sup> Normally p-doped SWNTs under the ambient conditions withdraw a valence electron from Co ion, creating positive charge on the molecule and negative charge on the nanotube. Organic molecules with large electron affinity or small ionization potential can also produce p-doped or n-doped SWNTs, respectively, through the electron transfer between the molecules and nanotubes.<sup>29</sup> In the addition to the van der Waals component, metallocenes and other redox active molecules are expected to have a significant electrostatic component in their interactions with SWNTs.

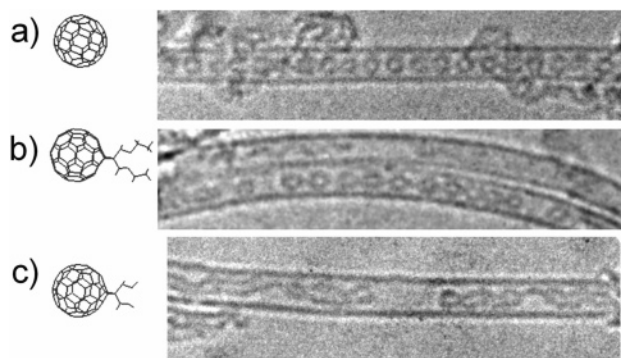
Octasiloxane,  $\text{Si}_8\text{H}_8\text{O}_{12}$ , is a cube-shaped molecule with a H-atom pointing outward from each corner of the cube (Figure 9). The diameter of  $\text{Si}_8\text{H}_8\text{O}_{12}$  is slightly smaller than that of  $\text{C}_{60}$ , so octasiloxane can enter narrower nanotubes than fullerenes. Hydrogen atoms of octasiloxane come in direct contact with the nanotube surface when the molecule is nested inside; the vibrational frequency of the Si–H bond normally appearing as a sharp band at  $2277\text{ cm}^{-1}$  in IR spectra in solution can be used for probing interactions between the octasiloxanes and the nanotube. Upon insertion, the Si–H absorption band is substantially broadened for  $\text{Si}_8\text{H}_8\text{O}_{12}$ @SWNT and its center is red-shifted by ca.  $-15\text{ cm}^{-1}$ . A shift opposite in sign ( $+17\text{ cm}^{-1}$ ) is observed for  $\text{H}_8\text{Si}_8\text{O}_{12}$  in the crystal, indicating that the molecules in  $\text{H}_8\text{Si}_8\text{O}_{12}$ @SWNT are not in a crystal-like state but in a state closer to solution. In nanotubes with diameters  $\sim 1.5\text{ nm}$ , most or all of the H-atoms of  $\text{H}_8\text{Si}_8\text{O}_{12}$  will be pointing toward the nanotube sidewalls so that  $\nu(\text{Si–H})$  will be directly affected by any

interaction between  $\text{H}_8\text{Si}_8\text{O}_{12}$  and the nanotube interior. Thus the most likely explanation for the shift of  $\nu(\text{Si}-\text{H})$  in SWNTs is the elongation of  $\text{Si}-\text{H}$  bonds as a result of dispersion forces acting between  $\text{H}_8\text{Si}_8\text{O}_{12}$  and the nanotube.<sup>30</sup> A large red shift was reported for NO-dimer adsorbed inside SWNTs as compared to NO-dimer in the gas phase,<sup>31</sup> which was also attributed to the strong interaction with the nanotube interior. The broadening may be attributed to different local environments for  $\text{Si}-\text{H}$  bonds depending on orientation of octasiloxane with the NT and with each other. This is confirmed by HRTEM, where we see a large degree of disorder of the  $\text{Si}_8\text{H}_8\text{O}_{12}$  in many of the nanotubes. In contrast *o*-carborane,  $(\text{CH})_2(\text{BH})_{10}$ , an icosahedral molecule decorated with H-atoms similarly to octasiloxane, was found to form zigzag packing in SWNTs.<sup>32</sup> Flat aromatic molecules of perylene derivative PTCDA were also demonstrated to be ordered within nanotubes in chains comprising stacked molecules in a face-to-face fashion probably resulting from a strong  $\pi-\pi$  interaction between the guest molecules.<sup>33</sup>

## Chemical Reactions inside Nanotubes

The examples presented above illustrate unambiguously that the structural and dynamic behavior of the molecules are substantially affected by confinement inside carbon nanotubes. A logical question to ask at this point would be, "how is the chemical reactivity of a molecule affected by the confinement?" The understanding of the mechanisms of the chemical reactions inside nanotubes is important and may lead to new applications of NTs as nanoscopic reactors. For example, the nanotube can be thought of as a shield around the molecules, lowering the activation barrier for some chemical reactions or favoring the formation of one isomer out of many possible in solution or in the solid state. Recent theoretical calculations predicted lowering of the activation barrier of Menshutkin  $\text{S}_{\text{N}}2$  reactions inside nanotubes.<sup>34</sup> Generally speaking, the selectivity and the yield of organic reactions carried out inside nanotubes can be expected to be better and higher than in solutions because of the isolated, strictly controlled environment inside nanotubes.

To use NTs as chemical reactors, three major steps should be demonstrated: (1) a reliable method for loading reactive molecules into NTs, (2) a well-defined chemical transformation inside nanotubes, and (3) retrieval of the reaction product from the nanotubes. Filling nanotubes with chemically reactive fullerenes remained a challenge for many years because the methods traditionally used for insertion of fullerenes into nanotubes involved the use of high temperature (300–600 °C) to ensure that the molecules are in the vapor phase and possess enough kinetic energy to enter the nanotubes.<sup>6,7</sup> Most organic molecules decompose below this temperature, making established techniques for insertion of fullerenes unsuitable. Recently, we found that supercritical  $\text{CO}_2$  acts as an efficient medium for transporting molecules into the nanotubes.<sup>35</sup>  $\text{scCO}_2$ , with the critical point just above room



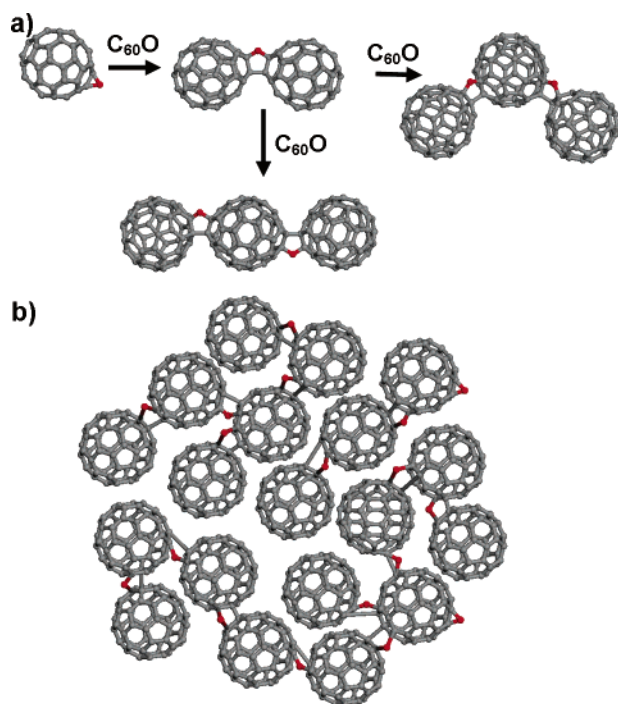
**FIGURE 10.** HRTEM micrographs of nanotubes filled with  $\text{C}_{60}$  (a) and functionalized fullerenes  $\text{C}_{61}(\text{COOEt})_2$  (b) and  $\text{C}_{61}(\text{COOH})_2$  (c).

temperature, appears to be highly efficient when a mixture of nanotubes and the fullerenes is immersed into the fluid under pressure 100–150 kbar.<sup>36</sup> Under these unusual conditions, the interactions between  $\text{C}_{60}$  molecules and  $\text{CO}_2$  can be controlled simply by changing the pressure: at lower pressure, the  $\text{scCO}_2-\text{C}_{60}$  interactions are attractive, which helps to solubilize  $\text{C}_{60}$ , whereas at high pressure the interactions are repulsive and cause the precipitation of  $\text{C}_{60}$  from solution. Because supercritical fluids have no surface tension, very low viscosity, and high diffusivity and because of the small critical diameter of the  $\text{CO}_2$  molecule,  $\text{scCO}_2$  does not block nanotubes, allowing  $\text{C}_{60}$  to enter into the nanotube cavities and the solvent molecules to escape from the NT. SWNTs were filled with  $\text{C}_{60}$  and its thermally unstable derivatives under pressure cycling conditions with a yield of up to 70%, substantially exceeding the yield obtained by using conventional solvents. Conventional organic solvents and water used in our experiments for filling arc-discharge nanotubes at room temperature produced only a small fraction of fullerene-filled nanotubes with most of the fullerene deposited on the nanotube surface. However, other researchers reported ethanol and hexane to be effective for insertion of  $\text{C}_{60}$  into SWNTs.<sup>37</sup>

Fullerenes functionalized with ester or carboxylic groups do not decay under the  $\text{scCO}_2$  filling conditions, and the  $\text{C}_{61}(\text{COOH})_2@\text{SWNTs}$  and  $\text{C}_{61}(\text{COOEt})_2@\text{SWNTs}$  were the first structures where reactive chemical groups were encapsulated in NTs, providing an opportunity for studying chemical reactions. The functionalized fullerenes appeared to be significantly less stable in the e-beam and decompose in several seconds while being imaged by HRTEM (Figure 10), whereas no structural changes are normally observed for unfunctionalized fullerenes and endohedral fullerenes under the same imaging conditions for at least 20 min.

The next step toward the realization of NTs as chemical reactors requires a molecule with well-known reactivity that can be transformed from a relatively inert state to a reactive state by external stimuli, such as light, heat, or an electrochemical potential. Such molecules can be inserted into NTs intact in  $\text{scCO}_2$ , and then the reaction between the molecules can be initiated. The nanotube interior is expected to be chemically inert (much less

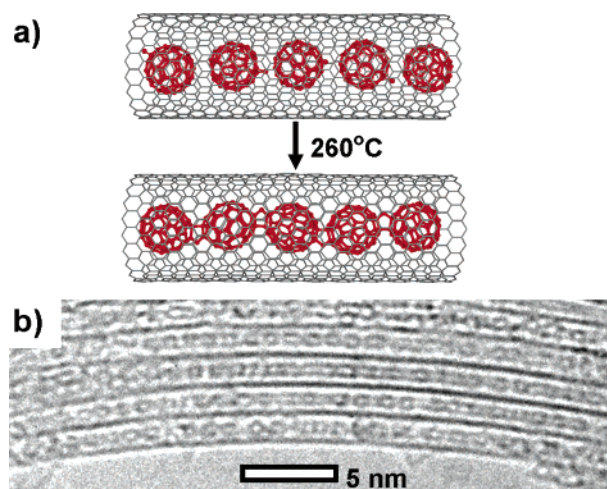




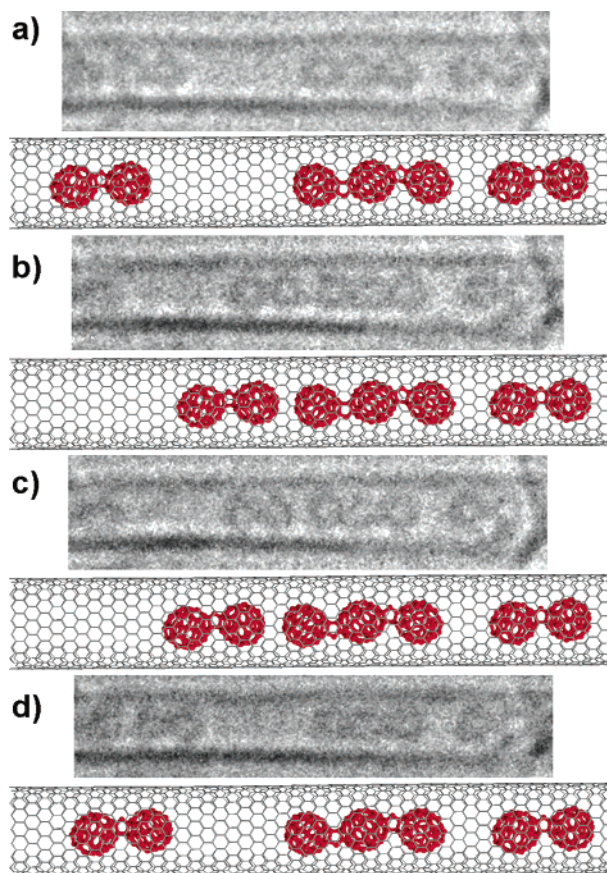
**FIGURE 11.** Polymerization of C<sub>60</sub>O (a) and schematic representation of (C<sub>60</sub>O)<sub>n</sub> polymer formed in the solid state (b).

reactive than the nanotube exterior), and therefore NTs should be, in principle, suitable for most chemical processes. Fullerene epoxide, C<sub>60</sub>O, is a stable molecule at room temperature, but above ~200 °C, the strained epoxide ring opens up and thus forms a highly reactive intermediate, which reacts with double C=C bonds to form furan rings (Figure 11a).<sup>38</sup> Because the monomeric C<sub>60</sub>O is merohedrally disordered in the crystal above room temperature (i.e., exists as a mixture of different orientations), the polymer (C<sub>60</sub>O)<sub>n</sub> (Figure 11b) forms in a disordered fashion when C<sub>60</sub>O is heated at 260 °C.<sup>39</sup> With the use of supercritical fluids, C<sub>60</sub>O was inserted into SWNTs, and a ring-opening polymerization was carried out inside the nanotube, yielding in (C<sub>60</sub>O)<sub>n</sub>@SWNT structures.<sup>40</sup> Fullerenes were observed to have regular periodicity, indicating that the C<sub>60</sub>O molecules bond to each other in a head-to-tail fashion, so all molecules would be aligned in the same direction when reacting (Figure 12).

When NTs are filled with a mixture of C<sub>60</sub> and C<sub>60</sub>O, then formation of oligomeric units such as C<sub>120</sub>O and C<sub>180</sub>O<sub>2</sub> is possible. The average length of the oligomer can in principle be controlled by the C<sub>60</sub>/C<sub>60</sub>O ratio with the higher ratio giving shorter oligomers and vice versa. In the case of sparsely filled SWNTs, it is possible to observe translational motion of dimers and other oligomers (Figure 13). The dimer and trimer translate freely in the SWNT: they move as isolated single molecules without dissociating and collide with each other without forming intermolecular bonds at ambient temperature in HRTEM. Bent rather than linear trimers C<sub>180</sub>O<sub>2</sub> (Figure 11a), form preferentially in solution<sup>41</sup> suggesting that linear trimers C<sub>180</sub>O<sub>2</sub> formed inside the nanotube during thermal treatment are a result of the nanotube templating action.<sup>42</sup>



**FIGURE 12.** Schematic representation of thermally activated polymerization of C<sub>60</sub>O inside nanotubes (a) and HRTEM micrographs of (C<sub>60</sub>O)<sub>n</sub>@SWNTs (b).



**FIGURE 13.** Time series of micrographs and corresponding structural diagrams of SWNT filled with oligomers C<sub>120</sub>O and C<sub>180</sub>O<sub>2</sub>.

Earlier research on filled carbon nanotubes showed how encapsulated molecules could be used to tune the functional electronic properties of the nanotubes. The field has since moved on to explore how the nanotubes can affect the encapsulated species. Nanotubes can be used as tiny chemical reactors with interactions between the molecules and the walls affecting the chemical behavior of the molecules. Studying intermolecular interactions in such small volumes could advance our understanding of

phase transitions of dimensionally confined environments and the mechanisms of chemical reactions. Nanotubes filled with biologically active molecules may be used as vehicles for drug delivery in living organisms. Encapsulation of electron spin or optically active endohedral fullerenes within SWNTs has also been proposed as an approach for the assembly of electronic nanodevices suitable for quantum information processing. We believe that there are opportunities for chemistry in carbon nanotubes that can change the way we make and manipulate molecules inside them.

*This research is part of the QIP IRC, www.qipirc.org (Grant GR/S82176/01), supported through the Foresight LINK Award Nanoelectronics at the Quantum Edge funded by DTI, EPSRC (Grant GR/R66029/01), and Hitachi Europe Ltd. A.N.K. is supported by the Leverhulme Trust, EPSRC, The Royal Society, and the University of Nottingham. D.A.B. is supported by an ORS Award. G.A.D.B. thanks EPSRC for a Professorial Research Fellowship (Grant GR/S15808/01).*

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AR040287V