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Azafullerenes Encapsulated within Single-Walled Carbon Nanotubes

Georgia Pagona,[†] Georgios Rotas,[†] Andrei N. Khlobystov,^{*,‡}
Thomas W. Chamberlain,[‡] Kyriakos Porfyrakis,[§] and Nikos Tagmatarchis^{*,†}

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 11635 Athens, Greece, School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, U.K., and Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, U.K.

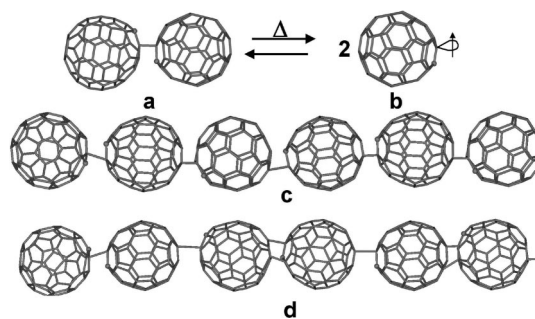
Received January 30, 2008; E-mail: tagmatar@eie.gr; andrei.khlobystov@nottingham.ac.uk

Almost a decade ago, when C_{60} fullerene molecules were inserted into single-walled carbon nanotubes (SWNTs) for the first time,¹ a new, exciting, and promising field of research was opened. Later on, endohedral metallofullerenes such as $Gd@C_{82}$,² other empty fullerene cages such as C_{70} and other higher fullerenes,³ as well as endohedral nitrogen fullerenes such as $N@C_{60}$ ⁴ have all been inserted into SWNTs,⁵ producing a great variety of “peapod” (i.e., carbon nanotubes filled with fullerene cages) nanostructures. Some of these hybrid structures are considered as potential materials for quantum information processing.⁶ Moreover, the spatial confinement of molecules inside SWNTs provides the opportunity to study the physico-chemical properties of molecules inside nanovessels.⁷ Recently, azafullerene $C_{59}N$ has also been encapsulated within SWNTs—either by using azafullerene derivatives $RC_{59}N$ as a precursor⁸ or by directly utilizing the parent bisazafullerene $(C_{59}N)_2$.⁹ However, in all cases, these peapod materials were prepared either in solution or in the gas phase and were characterized mainly by Raman spectroscopy.

In this study, we investigate methods of insertion of azafullerenes in SWNTs at different temperatures and explore the effects of the conditions applied on the structure of azafullerene-based peapods, $C_{59}N@SWNTs$, as compared with the traditional gas-phase, high-temperature procedure. We assess and evaluate the morphological characteristics of the hybrid material, $C_{59}N@SWNTs$, by means of high-resolution transmission electron microscopy (HR-TEM) and examine possible pathways and chemical reactions that occur upon encapsulation of $C_{59}N$ within SWNTs.

Under ambient conditions, in the crystal or in solution, azafullerene exists as a dimer of two cages linked by a single C—C bond (Scheme 1a). An HPLC purified $(C_{59}N)_2$ (10 mg) prepared from the cluster-opened N-MEM-substituted [60]-ketolactam (MEM: methoxy-ethoxy-methyl) according to published procedures¹⁰ was placed in one leg of a V-type quartz apparatus, while in the other leg 5 mg of purified open-ended SWNTs (Nanocarblab, Moscow, Russia; nominal tube diameter is 1.4 nm with a Gaussian width of 0.1 nm) was introduced. The system was degassed at 100 °C under dynamic vacuum conditions (10^{-5} – 10^{-6} Torr) for 60 min, sealed under vacuum, and then heated at 520 °C for 72 h. Figure 1 demonstrates representative HR-TEM images of such azafullerene peapods. The imaging conditions were set to minimize knock-on damage

Scheme 1. Structural Diagrams of (a) Bisazafullerene $(C_{59}N)_2$, (b) Azafullerenyl Radical $C_{59}N^*$, and (c, d) Proposed Oligomer $(C_{59}N)_n$



commonly occurring in peapod structures under exposure to the electron beam.¹² The accelerating voltage was set at 100 kV, the beam current on the specimen was reduced to minimum, and exposure times were 1–2 s to minimize the damage. Imaging under these conditions showed no structural changes in the examined azafullerene peapods over 10 min. As a first observation, the filling of the SWNTs with azafullerene cages is high (>90% of nanotubes are filled; Figure 1a). However, closer and careful inspection of these peapod structures reveals various morphologies for the encapsulated molecules. Specifically, monomers, dimers, and oligomers of azafullerene $C_{59}N$ cages were found inside SWNTs. In some nanotubes, the encapsulated azafullerene spheres seem intact (Figure 1b), while the center-to-center spacing is at 1.00 nm, thus corresponding to the monomeric form of $C_{59}N$. However, in other nanotubes, a center-to-center spacing of around 0.75 nm is observed for neighboring fullerene cages, indicating the presence of $(C_{59}N)_2$ dimers inside SWNTs (Figure 1c). Another type of molecular morphology observed in nanotubes corresponds to azafullerene

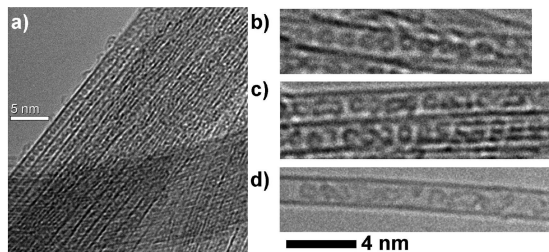


Figure 1. Representative HR-TEM micrographs of azafullerene peapods, prepared at 520 °C, illustrating (a) high filling rate and the presence of (b) monomers $C_{59}N$ stabilized in the interior of SWNTs, (c) dimers $(C_{59}N)_2$, and (d) oligomers of azafullerene cages.

[†] National Hellenic Research Foundation.

[‡] University of Nottingham.

[§] University of Oxford.

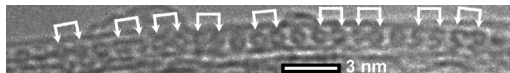


Figure 2. Representative HR-TEM micrographs of azafullerene peapods prepared in scCO_2 , at 50 °C. The double arrows indicate positions of dimer $(\text{C}_{59}\text{N})_2$ molecules inside the SWNTs, while some monomeric C_{59}N are also present.

oligomers where fullerene molecules appear to coalesce into a semiamorphous structure (Figure 1d).

At the temperature of 520 °C, when the filling of SWNTs with azafullerene takes place in the gas phase, the C—C interfullerene bond in bisazafullerene $(\text{C}_{59}\text{N})_2$ molecule dissociates, generating two azafullerenyl radicals $\text{C}_{59}\text{N}^\bullet$ (Scheme 1b).¹¹ Once inside SWNTs, three different scenarios for $\text{C}_{59}\text{N}^\bullet$ are possible, namely, (i) stabilization of the azafullerenyl radical $\text{C}_{59}\text{N}^\bullet$ in the interior of SWNTs, which is possible due to the isolation from the external environment (cf. Scheme 1b and Figure 1b), (ii) recombination of two $\text{C}_{59}\text{N}^\bullet$ radicals forming bisazafullerene $(\text{C}_{59}\text{N})_2$ (cf. Scheme 1a and Figure 1c), and (iii) bonding of $\text{C}_{59}\text{N}^\bullet$ to a neighboring $(\text{C}_{59}\text{N})_2$ molecule, transferring the unpaired electron to another azafullerene cage and, thus, initiating an oligomerization reaction (cf. Scheme 1c and/or d and Figure 1d). For the latter, we propose that an azafullerenyl radical $\text{C}_{59}\text{N}^\bullet$ attacks a dimer $(\text{C}_{59}\text{N})_2$ species, thus transferring the unpaired electron to the middle cage. Then, in the confined space inside SWNTs, another $\text{C}_{59}\text{N}^\bullet$ comes to associate to the third azafullerene cage forming another radical; however, due to the confinement inside SWNTs, branched oligomerization is not possible. This process continues with the following scenarios. Either all encapsulated azafullerenyl cages, apart from the first and last ones, incorporate an unpaired electron stabilized by the internal walls of SWNTs, isolated from the exterior environment (Scheme 1c), or as the unpaired electrons within the azafullerenyl oligomer are unlikely to stay in a fixed position, an unpaired electron is likely due to the conjugation of C=C bonds in the C_{59}N cage to migrate to a side of the cage nearest to the unpaired electron on the neighboring C_{59}N due to a spin—spin coupling. The two unpaired electrons will pair up, probably forming an additional C—C bond between the cages. This is to say that some C_{59}N cages within the oligomer will be linked by a single C—C bond and some by two single C—C bonds, as proposed in Scheme 1d. The latter might also partially explain why the oligomers appear to be unstable as C_{59}N cages linked by two C—C bonds are more likely to amalgamate under the electron beam during TEM observation. Importantly, SWNTs act as a container for the molecules and as a quasi-1D template allowing formation of only linear oligomers $(\text{C}_{59}\text{N})_n$ (whereas oligomers/polymers formed in the bulk can be curved and branched).¹³ Overall, the experimental HR-TEM images indeed confirm that all three reaction pathways for azafullerenyl radical $\text{C}_{59}\text{N}^\bullet$ take place inside nanotubes.

We have also successfully encapsulated azafullerene into nanotubes using a method utilizing supercritical CO_2 at 50 °C and a pressure cycle between 100 and 150 atm.¹⁴ Under such low-temperature—high-pressure conditions, a moderate filling rate, as compared with the traditional high-temperature gas-phase azafullerene encapsulation, was achieved. However, HR-TEM imaging of this sample shows that the majority of bisazafullerene molecules (cf. Scheme 1a) remain intact, as indicated by the high abundance of $(\text{C}_{59}\text{N})_2$ dimers within SWNTs (Figure 2). The center-to-center spacing between the neighboring fullerene cages is in the range of 0.75–0.82 nm for this sample, which is significantly shorter than the van der

Waals separation generally observed for fullerenes such as C_{60} (approximately 1.00 nm). This observation can be explained by the fact that at lower temperatures bisazafullerene exists as a dimer species which can enter SWNTs from supercritical CO_2 without dissociation, whereas at high temperature (520 °C) bisazafullerene dimers have to break up into monomeric units of C_{59}N , during sublimation, in order to enter SWNTs from the gas phase.

In summary, we have shown that monomeric azafullerenyl radical $\text{C}_{59}\text{N}^\bullet$ inserted into carbon nanotubes at high temperature, from purified $(\text{C}_{59}\text{N})_2$ in the gas phase, can undergo a variety of different transformations forming dimers, oligomers or existing in its monomeric form inside SWNTs due to the stabilization effect by nanotube side walls. Similar stabilization of monomeric azafullerene was previously demonstrated via bonding of C_{59}N to a semiconductor¹⁵ or a metal¹⁶ surface. However, under milder conditions (i.e., lower temperature), bisazafullerene $(\text{C}_{59}\text{N})_2$ can be inserted into nanotubes in its pristine dimeric form, which potentially can be used to generate free radical $\text{C}_{59}\text{N}^\bullet$ species, isolated from the external environment, for subsequent chemical reactions in a confined space inside SWNTs.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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