

Dynamics of Paramagnetic Metallofullerenes in Carbon Nanotube Peapods

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ABSTRACT

We filled SWNTs with the paramagnetic fullerene Sc@C₈₂ to form peapods. The interfullerene 1D packing distance measured using TEM is $d = 1.1 \pm 0.02$ nm. The Sc@C₈₂ in SWNT peapods continuously rotated during the 2 s TEM exposure time, and we did not see the Sc atoms. However, Sc@C₈₂ metallofullerenes in MWNT peapods have periods of fixed orientation, indicated by the brief observation of Sc atoms. La@C₈₂ peapods were also prepared and their rotational behavior examined. The interfullerene 1D packing of both La@C₈₂ and Sc@C₈₂ peapods is identical and thus independent of the charge transfer state for these paramagnetic fullerenes. The La@C₈₂ metallofullerenes in the peapods have fixed orientations for extended periods of time, up to 50 s in some cases. The La@C₈₂ spontaneously rotates rapidly between fixed orientations.

Single walled carbon nanotubes (SWNTs) have chirality dependent metallic and semiconducting behavior that can be exploited in nanoelectronic devices.¹⁻⁴ The semiconducting properties of SWNTs can be modified by inserting molecules such as fullerenes into their hollow interior to form peapod structures.^{5,6} Inserting metallofullerenes such as Gd@C₈₂ and Dy@C₈₂ alters the band gap of the SWNTs, and this in turn leads to changes in the conductivity of single SWNT peapod field effect transistors.⁷⁻¹⁰

The metal atom in the paramagnetic fullerene species Sc@C₈₂,¹¹ Y@C₈₂,¹² and La@C₈₂¹³ donates electrons to the

C₈₂ cage, resulting in an unpaired electron partially delocalized on the fullerene cage. Interaction of the unpaired electron with the dopant metal nucleus leads to narrow hyperfine splitting in the ESR that is dependent upon the nuclear spin of the metal dopant.¹⁴ These paramagnetic metallofullerenes have long spin coherence times and therefore are capable of embodying quantum information and are candidates as spin-based quantum bits (qubits).¹⁵

One dimensional (1D) chains of spins^{16,17} can be made by inserting spin-active fullerenes¹⁸ into SWNTs to form spin-chain peapods with regular packing arrangement along the nanotube axis.¹⁹ The use of peapods as 1D spin chains is still in its infancy, and its further development is critical for the future of spin-based carbon nanomaterial quantum information processing. Underpinning this development is the fabrication and understanding of suitable peapod structures and their characterization.

In this report, we demonstrate the production of a new type of peapod system involving the paramagnetic metal-

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lofullerene, Sc@C₈₂, and characterize it using high resolution transmission electron microscopy (HRTEM) at low accelerating voltages.²⁰ Characterization of the motion, rotation, orientation, packing dynamics, and structural stability of spin-active metallofullerenes in SWNT peapods is essential.²¹ Most investigations into the production of peapods have involved using nonparamagnetic metallofullerenes,^{22–27} with only one report of preparing La@C₈₂ peapods.²⁸ We also report the production of La@C₈₂ peapods for comparison with Sc@C₈₂ and provide an in-depth study into the rotational dynamics of the fullerenes within the SWNT peapods. While both La@C₈₂ and Sc@C₈₂ are paramagnetic and have excellent long-lived spin-states, they differ in their nominal charge transfer states.^{3–14} This allows a direct comparison between 1D spin-chains of paramagnetic metallofullerenes with different charge states and reveals different interactions within the SWNTs. We also explore the possibility of modifying the metallofullerene–nanotube interaction and consequently the rotational behavior of Sc@C₈₂ in peapods by using multiwalled carbon nanotubes (MWNTs) instead of single walled carbon nanotubes.

La@C₈₂ and Sc@C₈₂ were prepared using the arc-discharge method.^{11,12,14} The metallofullerenes were then isolated using multistage HPLC.¹⁴ SWNTs were Carboxylated nanotubes, produced using the arc-discharge method and purchased from Sigma Aldrich. The SWNTs were purified by annealing in air at 300 °C for 2 h, followed by microwave irradiation for 5 min and then refluxing in a 37% HCl solution for 6 h. This process was repeated four times.

Metallofullerene peapods were prepared by heating the purified SWNTs in air at 420 °C for 20 min to open their ends. Next, an appropriate amount of either La@C₈₂ or Sc@C₈₂ in CS₂ solution was dropped onto the SWNTs to coat them with metallofullerenes. The CS₂ was evaporated off, and the composite material was sealed under vacuum in a quartz tube and heated at 450 °C for 4 days. After 4 days, peapods were formed and washed with CS₂ and then finally dispersed in 1,2-dichloroethane using ultrasonication. TEM samples were prepared by dropping 1,2-dichloroethane solutions onto lacey carbon-coated TEM grids and allowing to dry. TEM was performed at 100 kV on a JEOL 4000EX transmission electron microscope equipped with a Gatan CCD camera.

The metallofullerenes were isolated by HPLC from soot generated using the arc-discharge process and were characterized by mass spectroscopy, UV–vis–NIR absorption spectroscopy, and electron spin resonance. MALDI-TOF mass spectroscopy confirmed that both La@C₈₂ and Sc@C₈₂ were highly purified, i.e., >95%. It has been well documented that both La@C₈₂ and Sc@C₈₂ are paramagnetic and have narrow ESR spectra associated with a partially delocalized unpaired electron on the C₈₂ cage, with hyperfine splitting due to interaction with the metal nucleus (Sc or La).^{11,13} The resulting ESR signal is a signature of both the metal dopant and the isomer of the C₈₂ cage. Different isomers of both Sc@C₈₂ and La@C₈₂ have been reported, and thus the combination of both ESR and absorption spectroscopy can confirm the isomer that has been isolated using HPLC.¹¹

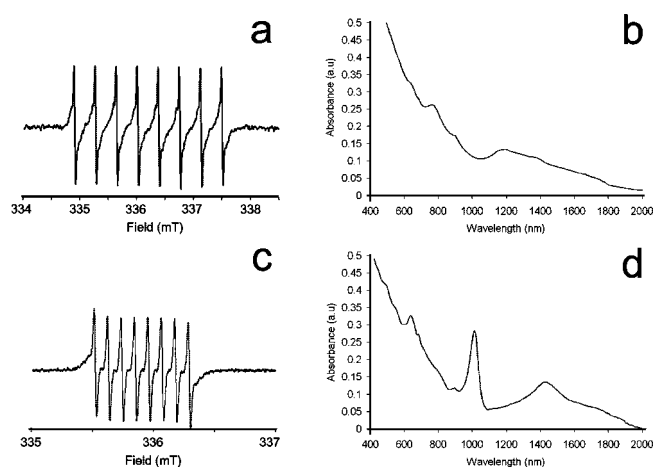


Figure 1. (a) ESR spectrum of purified Sc@C₈₂ (I), (b) UV–vis–NIR absorption spectrum of Sc@C₈₂ (I) in CS₂, (c) ESR spectrum of purified La@C₈₂ (I), (d) UV–vis–NIR absorption spectrum of La@C₈₂ (I) in CS₂.

Figure 1a shows the ESR signal of the purified Sc@C₈₂ metallofullerenes, and this matches the Sc@C₈₂ (I) isomer.¹¹ This is confirmed in the UV–vis–NIR absorption spectrum of the Sc@C₈₂ in CS₂, shown in Figure 1b, which also matches the Sc@C₈₂ (I) isomer.¹⁴ Figure 1c shows the ESR signal of the purified La@C₈₂, and this matches the La@C₈₂ (I) isomer.¹⁴ This is confirmed in the UV–vis–NIR absorption spectrum in Figure 1d, which also matches the La@C₈₂ (I) isomer.¹⁴

The highly purified La@C₈₂ (I) and Sc@C₈₂ (I) metallofullerenes were inserted into purified SWNTs using the well-established hot filling method for metallofullerene peapods.^{21–28} The peapod structures were analyzed using TEM, operating at 100 kV. By lowering the accelerating voltage, the knock-on damage of the carbon nanomaterials can be minimized.²¹ Figure 2a shows a TEM image of a bundle of Sc@C₈₂ SWNT peapods and reveals a high degree of filling. In Figure 2b, a higher magnification TEM image shows the filling of the SWNTs with Sc@C₈₂ metallofullerenes and these are densely packed within the SWNTs. In Figure 2c, what appears to be the end of several Sc@C₈₂ peapods in a bundle are imaged. We determined that this was the end of the peapod bundle by following the bundle from the beginning to this end point when investigating with TEM. In the higher magnification image, presented in Figure 2d, the end of the SWNTs can be seen to be filled with a metallofullerene, forming a double ring as indicated by an arrow. This shows that the ends of the SWNTs have been opened and the metallofullerenes easily enter the SWNTs to form densely packed peapods. A large number of bundles and individual SWNTs were examined using TEM and allowed an estimation of the filling percentage to be 70–90%. The high degree of filling enabled the average interfullerene spacing of the Sc@C₈₂ in the SWNT peapods to be measured using fast Fourier transform (FFT) analysis of TEM images. Figure 2e shows the FFT taken from the TEM image in Figure 2a. The lines labeled *a* and *b* are due to the regular 1D packing of the Sc@C₈₂ in the SWNTs. From this FFT analysis, the average center-to-center interfullerene spacing

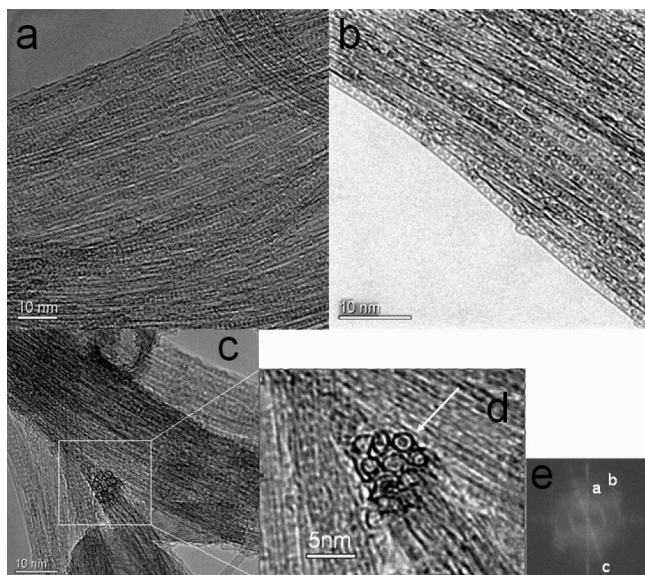


Figure 2. (a) TEM image of a bundle of Sc@C₈₂ SWNT peapods, (b) higher magnification of Sc@C₈₂ SWNT peapods, (c) and (d) TEM images showing the ends of a rope of Sc@C₈₂ peapods, (e) FFT from TEM image shown in Figure 2a.

is calculated to be $d = 1.1 \pm 0.02$ nm. This technique has been verified for accuracy by analyzing peapods containing C₆₀. FFT analysis of the C₆₀ peapods measured interfullerene distances of 0.97 nm, which matches previously reported values.²⁹

Information regarding the molecular motion and rotation of the Sc@C₈₂ metallofullerenes in the SWNT peapods can be obtained using high resolution transmission electron microscopy. Increased contrast from the metal dopant in the metallofullerene as compared to carbon can allow the direct observation of the rotational dynamics within the SWNT.^{21,28} In most monometallofullerenes, the metal dopant lies off-center and close to the fullerene cage, allowing the possible observation of rotation and orientation in the corresponding peapod structures.^{21,28} The observation of metal atoms in the peapods is critically dependent upon the rotation dynamics of the metallofullerenes. If the rotational is rapid and continuous during the image acquisition, then it is difficult to locate the metal atom.²⁴ However, if the metallofullerene remains fixed in a specific orientation for a time comparable to the image acquisition time, then the metal dopant can be observed.

Parts a and b of Figure 3 show HRTEM images of isolated single Sc@C₈₂ SWNT peapods. The observation of higher contrast spots due to the presence of Sc metal dopants was not apparent. This indicates that the rotation of the Sc@C₈₂ within the peapod is rapid and continuous during the 2 s time scale over which the exposure was taken. Reduced exposure times were explored, but the resulting image quality was insufficient to extract any valuable information. Many other isolated single peapods and peapod bundles were examined, all showing no signs of any periods of fixed orientation. This agrees well with other observations of peapods containing metallofullerenes with similar nominal charge transfer such as Sm@C₈₂.²⁴ In this case, the rotation

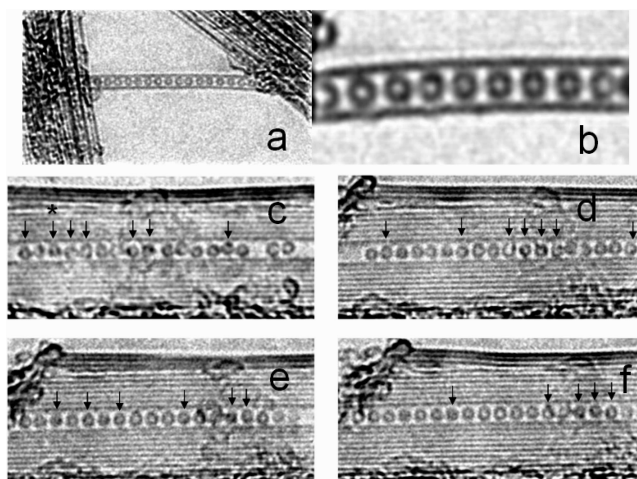


Figure 3. (a) TEM image of an isolated Sc@C₈₂ SWNT peapod, (b) HRTEM image of an isolated Sc@C₈₂ SWNT peapod, (c–f) HRTEM images of Sc@C₈₂ MWNT peapod.

of the Sm@C₈₂ metallofullerene was continuous and prevented the observation of the Sm metal dopant.²⁴

The results are found to be different when examining peapods made with Sc@C₈₂ inside multiwall carbon nanotubes (MWNTs). Within the ensemble of Sc@C₈₂ peapods, there were several MWNT peapod samples that were examined using HRTEM. TEM analysis revealed the ends of the MWNTs were opened during the oxidative annealing and acid etching purification processes, allowing the metallofullerenes to enter inside (see Supporting Information). Parts c–f of Figure 3 show the Sc@C₈₂ metallofullerenes inside a MWNT with 11 concentric tubes. The majority of Sc@C₈₂ metallofullerenes have continuous rotation in the MWNTs, but several of the Sc@C₈₂ metallofullerenes exhibited periods of fixed orientation, allowing the observation of the Sc atom for a brief period. In Figure 3c, a metallofullerene is observed to have two distinct spots, indicated by *. This type of observation is attributed to a metallofullerene rotating rapidly between two stable orientations within the 2 s exposure time taken to acquire the image, similar to other reports on Ce@C₈₂ peapods.²¹

These results indicate that there is a change in the rotational dynamics of the Sc@C₈₂ in the MWNTs compared to the SWNTs. The MWNTs in this ensemble sample were observed to have similar internal diameters as the SWNTs but with an increase in the number of graphene layers. This suggests that the nanotube environment plays a significant role in the rotational freedom of Sc@C₈₂ metallofullerenes in peapods. The change from a single graphene sheet in a SWNT to 11 graphene sheets in the MWNT has effectively modified the rotational dynamics of the system by changing the metallofullerene–nanotube interaction. This type of interaction is dominated by the van der Waals interaction, which is dependent upon the nature of the carbon nanotube structure and local environment. The van der Waals forces arise from interactions between instantaneous dipole fluctuations of the polar Sc@C₈₂ and the nonpolar carbon nanotube. The larger electron cloud in the 11 graphene layers of the MWNT, as compared to the SWNT, has increased polariz-

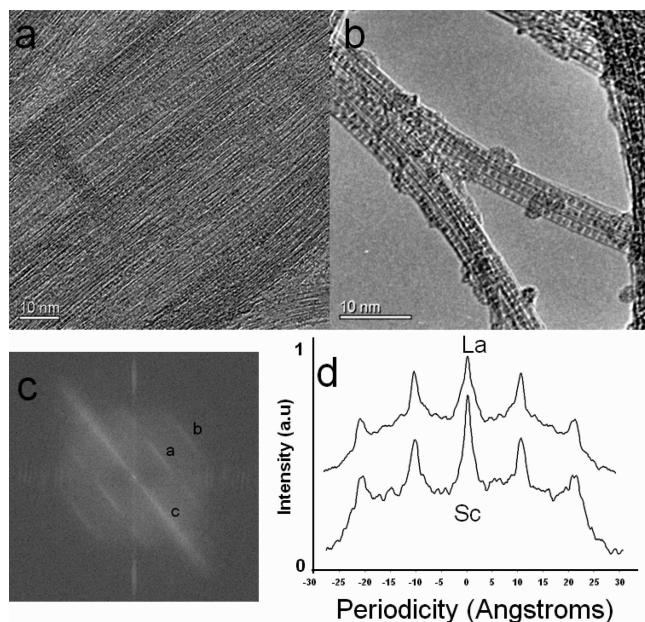


Figure 4. (a) TEM image of a bundle of La@C₈₂ peapods, (b) higher magnification TEM image of a rope of La@C₈₂ peapods, (c) FFT taken from Figure 4a, comparison of the FFT profiles of La@C₈₂ and Sc@C₈₂ peapods, which plots FFT intensity as a function of periodicity.

ability, and this leads to stronger van der Waals forces between the Sc@C₈₂ and MWNT, which could explain the changes in rotational dynamics of the Sc@C₈₂ and the observation of periods of fixed orientation.

The TEM images in parts c–f of Figure 3 also show that the Sc@C₈₂ has translational mobility within the MWNT and is free to exhibit 1D lateral motion along the inside of the nanotube.²¹ This provides further conclusive evidence that the Sc@C₈₂ is inside the inner tube of the MWNT peapod. Successive HRTEM images of the Sc@C₈₂ MWNT peapods were taken to ensure that the reduced rotation was not an effect of electron beam damage. We found that Sc@C₈₂ metallofullerenes that had become rotationally frozen for a short period of time were then able to continue rotating. Thus, the observation of the Sc atom within the Sc@C₈₂ was only temporary and not long-term. This confirms that the observation of reduced rotation rate is not due to electron beam damage.

La@C₈₂ peapods were also prepared and it is expected that these metallofullerenes will have different dynamics than Sc@C₈₂ inside the SWNT peapods due to the increase in charge transfer. A previous report of La@C₈₂ peapods showed the presence of a high contrast region in the metallofullerenes, which was attributed to the La metal atom.²⁸ The orientation of individual La@C₈₂ metallofullerenes in the peapods was measured, but the rotation dynamics and changes in the orientation of the La@C₈₂ with time were not studied.²⁸ Rotational dynamics of Ce@C₈₂ metallofullerenes in SWNT peapods also show periods of fixed orientation.²¹

Figure 4a shows a TEM image of a large bundle of SWNTs filled with La@C₈₂ to form peapods. A high degree of filling was observed for the La@C₈₂ peapods, estimated

to be 70–90%. Figure 4b shows a TEM image of higher magnification, and the individual La@C₈₂ metallofullerenes can be observed within the SWNTs. An FFT was taken from the TEM image of the bundle of La@C₈₂ peapods in Figure 4a and is shown in Figure 4c. Similar to the FFT of the Sc@C₈₂ peapods shown in Figure 2e, two sets of lines corresponding to the 1D regular packing of the La@C₈₂ in the SWNTs are apparent. This allows the average interfullerene La@C₈₂ distance to be calculated as $d = 1.1 \pm 0.02$ nm. This interfullerene 1D packing of the La@C₈₂ in SWNT matches the Sc@C₈₂ 1D packing distance. Figure 4d shows the line profile taken from the FFT and plots the FFT intensity as a function of periodicity. The intensity of the FFT is a measure of the frequency of occurrences of repeated spatial periodicity in the TEM image. The more frequently the spatial periodicity occurs, the higher intensity the FFT line will be. This allows a direct comparison between the FFT profile of the La@C₈₂ and Sc@C₈₂ 1D packing in peapod structures. The two profiles in Figure 4d show a high degree of correlation between the packing, even though the Sc@C₈₂ and La@C₈₂ have different charge transfer states. This indicates that the interfullerene 1D packing of paramagnetic metallofullerenes in SWNT is not dependent upon their charge state, in agreement with previous studies that found similar interfullerene packing distances for several metallofullerenes with C₈₂ carbon cages in SWNT peapods.²⁹

Finally, the time dependent orientation of the La@C₈₂ metallofullerenes in SWNTs is examined. Single isolated La@C₈₂ peapods were imaged with HRTEM using a 2 s exposure time and 10 s between successive images. Figure 5i shows a time series of TEM images from a La@C₈₂ peapod section containing three metallofullerenes, with the last image taken almost 100 s after the first. Three isolated La@C₈₂ metallofullerenes are visible within the SWNT, along with the high contrast spots that indicate the location of the La atom and the orientation of the La@C₈₂ with respect to the axis of the SWNT. A schematic representation is presented to the right of each TEM image to illustrate the orientation of the metallofullerenes. As time progresses, each metallofullerene remains in a fixed orientation for a period of time before rapidly switching to another stable orientation. The switching time between fixed orientations is generally faster than the 2 s acquisition time. However, in i and j, we observed two spots in a La@C₈₂ metallofullerene (marked with *). In these cases, the orientation of the La@C₈₂ changed between two fixed positions during the 2 s, similar to the observations of Sc@C₈₂ in MWNT peapods. Other isolated single peapods containing La@C₈₂ were analyzed with HRTEM and showed similar behavior (see Supporting Information).

The time dependence of the orientation of each metallofullerene (1, 2, and 3) in Figure 5i, with respect to the axis of the SWNT, was measured for 125 s and showed little correlation between neighboring fullerenes (see Supporting Information). We found that the time-dependent orientation behavior of each metallofullerene was different. Two remained stable in fixed orientations for long periods, while the other changed its orientation regularly over the 125 s.

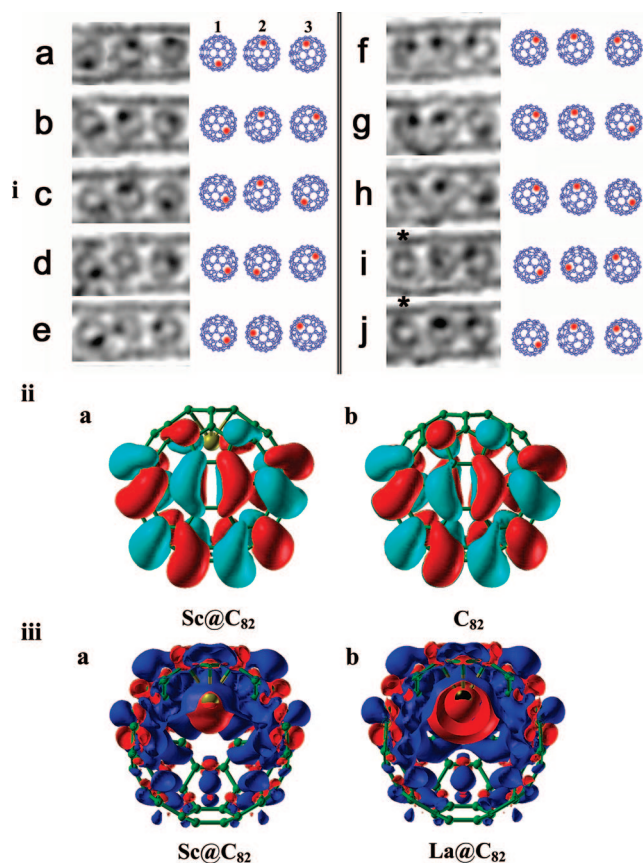


Figure 5. (i) Time-series of TEM images taken from sections of La@C₈₂ peapods containing 3 metallofullerenes. Images were taken with 2 s exposure and 10 s intervals. Schematic representation of the metallofullerene orientation is presented to the right of each image. (ii) (a) LUMO of relaxed Sc@C₈₂. (b) (LUMO + 2) of relaxed C₈₂ (C_{2v}). Red and cyan lobes represent positive and negative phases. (iii) Charge transfer in (a) Sc@C₈₂ and (b) La@C₈₂ metallofullerenes. Values for red and blue surfaces are ± 0.003 e/Å³. The atom colored in gold (black) is Sc (La).

The time dependence of the distance between the La atoms for metallofullerenes 1 and 2 (d_{1-2}) and for 2 and 3 (d_{2-3}) was measured and showed some degree of correlation (see Supporting Information), i.e., changes in d_{1-2} were reflected in the changes in d_{2-3} .

Monitoring the orientation of the metallofullerenes over time provides a deeper insight into their interactions. The La@C₈₂ metallofullerenes maintained stable orientations for long periods of time and then spontaneously rotated to another stable orientation in a rapid time scale. During the TEM observation of the La@C₈₂ peapods, minimal damage to the metallofullerenes was inflicted due to the relatively low energy (100 kV) and irradiance of the electron beam. Damage of metallofullerenes leads to the atomic migration of the metal atom being expelled from the fullerene cage, and this can alter the apparent rotational properties.³⁰ We did not observe this phenomenon while imaging the La@C₈₂ peapods for several minutes, but after this initial period of time, damage started to become apparent. The studies presented in this report were conducted and completed within the time scale before damage started to be inflicted. Isolated peapods suspended between two bundles were examined in order to prevent interactions with neighboring peapods from

influencing the results. These results agree well with previous reports of peapods containing metallofullerenes with similar charge transfer, i.e., Gd@C₈₂ and Ce@C₈₂. In these cases, the metal dopant was imaged in HRTEM and their behavior examined.^{19,21}

The rotation and orientation dynamics of metallofullerenes in peapods are influenced by the exchange interactions and electrostatic dipole–dipole interactions between metallofullerenes, van der Waals forces between metallofullerenes and nanotubes, and the effect of electron beam irradiation during TEM. The interaction between metallofullerenes in peapods is dependent upon the electronic charge distribution of both the ground and excited states.

Both Sc and La have three valence electrons. In Sc@C₈₂, two of the three valence electrons form bonding orbitals with C₈₂ and the unpaired electron occupies the highest occupied molecular orbital (HOMO) and delocalizes over the C₈₂ cage, which is in agreement with previous results.^{31,32} Our density functional theory (DFT) calculations show that the HOMO and lowest unoccupied molecular orbital (LUMO) of Sc@C₈₂ are virtually identical to the (LUMO + 1) and (LUMO + 2) of C₈₂ (C_{2v}), respectively, as shown in Figure 5ii. Similar results have been obtained for La@C₈₂.³³ Figure 5iii shows the electronic charge rearrangement following the metal atom (Sc or La) encapsulation in the C₈₂ cage. The electron depletion from the metal La atom is larger than Sc, with correspondingly larger electron accumulation on the surrounding carbon atoms. This leads to a rather large dipole moment for La@C₈₂.³⁴ Large electrical dipole moments have been previously postulated to describe the orientation behavior in a 1D chain of Ce@C₈₂ and La@C₈₂ metallofullerenes in a peapod.^{21,28} We conjecture a similar effect here. If the electric dipole moment of La@C₈₂ is larger than the electric dipole moment of Sc@C₈₂, it would give greater coupling between the fullerenes in the peapod. The electron beam causes individual fullerene molecules to become charged. This provides electrostatic forces to cause translational motion, as has been conjectured in C₆₀ peapods.³⁵ The electron beam may also excite higher electronic states, and the resulting change in electron distribution may modify the interactions.

The excitation of electrons from ground-state molecular orbitals (HOMO, HOMO – 1, and HOMO – 2) containing significant Sc or La character to higher energy orbitals could lead to a modification of the dipole moment in the metallofullerenes. Our DFT calculations have shown that the manifold of excited states varies significantly between Sc@C₈₂ and La@C₈₂, and this is confirmed by examining the different profiles obtained in the optical absorption spectra in Figure 1. The charge distribution for excited states are delocalized over the fullerene cage, whereas the lower-lying states that are responsible for bonding with the metal atom are more localized. The rotation of metallofullerenes between positions of fixed orientation is possibly influenced by the fluctuations in the strength of the dipole moment, caused by excitation. Electron beam irradiation might even provide an addressable means to drive rotations and translations of metallofullerenes in peapods for bucky-shuttle memory

devices.^{36–38} The atomic mass of La (138.90 g·mol^{−1}) is larger than that of Sc (44.96 g·mol^{−1}) and hence may require a greater angular impulse to change the orientation of a fullerene containing it.

In any future use of peapods for quantum nanotechnologies, it will be essential to understand factors affecting the orientation of fullerenes and their interaction with each other as well as with the nanotube in which they are assembled. By comparing the behavior of Sc@C₈₂ and La@C₈₂ peapods, we can deduce that the intermetallofullerene interactions, which depend on charge transfer, play a major role in the dynamics of the system, along with the metallofullerene–nanotube interactions. This has important implications toward the future utilization of peapods for quantum information processing of spin chains.

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Supporting Information Available: Computational details. TEM image of the open end of a MWNT peapod containing Sc@C₈₂ metallofullerenes. Schematic diagram showing how the orientation of metallofullerenes with respect to the axis of the SWNT was measured. Time dependence of the orientation angle for La@C₈₂ metallofullerene number 1. Time dependence of the orientation angle for La@C₈₂ metallofullerene number 2. Time dependence of the orientation angle for La@C₈₂ metallofullerene number 3. Time dependence of the distance between La atoms for metallofullerenes 1–2, and 2–3. Time-series of HRTEM images of La@C₈₂ SWNT peapods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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