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Selective host–guest interaction of single-walled carbon nanotubes with functionalised fullerenes

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Exohedrally functionalised fullerenes have been inserted in single-walled carbon nanotubes (SWNTs) with the aid of supercritical carbon dioxide to form peapods; $C_{61}(COOEt)_2$ are encapsulated in SWNTs in high yield, whereas $C_{61}(COOH)_2$ aggregate *via* hydrogen bonding to form a supramolecular complex, which sterically hinders encapsulation and causes it to adhere to the exterior surface of the SWNTs.

It has been well demonstrated that fullerenes, such as C_{60} **1** and C_{70}, readily enter single-walled carbon nanotubes (SWNTs) in the gas phase to form so-called 'peapod' structures (Fig. 1a), designated as C_n@SWNT.[1] Endohedral metallofullerenes (EMFs)—a class of carbon cages encapsulating one or several atoms—can also enter carbon nanotubes in high yield at elevated temperatures, presumably by surface diffusion of the EMFs along the surface of the SWNT.[2] The host–guest interactions in the 'peapod' structures are mediated by highly effective van der Waals interactions common for sp^2-carbon materials.[3]

Exohedrally functionalised fullerenes (to be referred to simply as "functionalised fullerenes"), bearing organic or organometallic functional groups attached to the exterior of the carbon cage, are a more diverse and accessible class of fullerene molecules than endohedral metallofullerenes. By exploiting fullerene cages as anchors that interact with nanotubes by strong van der Waals forces,[3] simple chemical transformations of the organic groups could enable the introduction of different chemical functionalities into SWNT cavities (Fig. 1). These structures containing chemically or electronically active functionalities inside SWNT could be useful for creating nanotube-based electronic devices, sensors, or bioactive nanostructures. Until now, functionalised fullerenes have not been inserted into SWNTs because their functional groups decompose at the temperatures generally used for filling empty fullerenes. Herein, we report a low temperature, high yielding filling technique for functionalised fullerenes and examine the influence of the nature of the functional group on the nanotube–fullerene host–guest interactions. We find that altering the functional group can enhance or inhibit encapsulation, as compared to pristine C_{60}.

The cyclopropafullerene-C_{60}-dicarboxylic acid diethyl ester **2**, $C_{61}(COOEt)_2$, and the cyclopropafullerene-C_{60}-dicarboxylic acid **3**, $C_{61}(COOH)_2$, were synthesised and purified using previously described methods.[4] SWNTs (Aldrich) were purified using literature techniques[5] to achieve two diameters of 1.3 nm and 1.5 nm. Based on extensive microscopy and Raman spectroscopy studies, the 1.5 nm and 1.3 nm SWNTs made up 70% and 30% of the sample, respectively. A five-fold excess of **1**, **2** or **3** was separately mixed with purified SWNTs in CS_2, and each mixture was dried in air and inserted into a high pressure cell. The fullerene–SWNTs mixtures were immersed in supercritical CO_2 ($scCO_2$) at 50 °C under 150 bar. The pressure of CO_2 was kept between 100–150 bar for several days to maintain supercriticality. Following the attempted filling process, each mixture was repeatedly sonicated in CS_2 (**1**, **2** and **3**) or MeOH (**3**), and then filtered to remove excess fullerene adsorbed to the outside of the SWNTs.

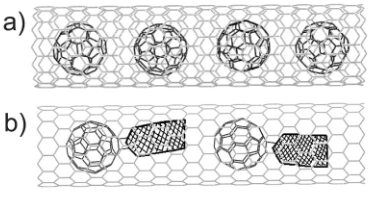

Fig. 1 Schematic diagrams of (a) C_{60}@SWNT and (b) a 'peapod' containing functionalised fullerenes (functional groups are represented by cross-hatched rectangles).

Supercritical conditions were chosen for nanotube filling because CO_2 is known to provide a clean, inert environment and does not solvate solute molecules,[6] potentially enabling effective encapsulation into nanoscopic cavities. The nanotube filling yield of each sample was extensively studied using high-resolution transmission electron microscopy (HRTEM). Imaging conditions were set to minimise knock-on damage,† which is a common problem in TEM characterisation of carbon nanostructures.[7] Generally, one hundred images from different areas of the specimen were observed† to determine the yield of peapods. C_{60} was found to fill 30% of the total number of tubes (Fig. 2a), with the wider tubes preferentially filled, while the narrower tubes remained empty. Interestingly, the filled nanotubes formed densely packed peapods, with fullerenes at the van der Waals' distance. It is possible that the unfilled tubes had partially blocked ends, inhibiting encapsulation of C_{60}.

$C_{61}(COOEt)_2$@SWNT peapod structures were formed in 60% yield of the total nanotubes observed. Again, the wide diameter nanotubes were preferentially filled, whereas the narrower nanotubes remained empty. Because the filling conditions for **1** and **2** were identical, the enhancement of filling is attributed to the presence of the diethyl ester functional groups. The functionalised fullerene cages appear to be more sensitive to the electron beam than non-functionalised fullerenes. The molecules of **2** become elongated under HRTEM imaging conditions in a few seconds,

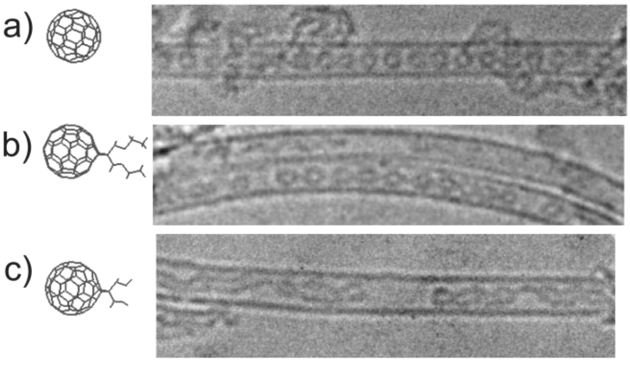

Fig. 2 HRTEM micrographs of (a) C_{60}@SWNT, (b) $C_{61}(COOEt)_2$@SWNT and (c) $C_{61}(COOH)_2$@SWNT structures showing the relative stability of functionalised fullerenes under an e-beam. The exposure time is 1 s for all images.

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which is followed by aggregation into polymeric chains (Fig. 2b). HRTEM also showed that the washing procedure was effective for removing non-encapsulated fullerenes from the nanotube surface, as fullerene-type structures were not observed outside the nanotubes. FT-IR spectra of $C_{61}(COOEt)_2$@SWNTs confirmed the presence of the functional groups inside SWNTs. Vibrational modes characteristic for ester C=O (1745 cm^{-1}) and ethyl C–H (2800–3000 cm^{-1}) groups can be observed superimposed on the broad SWNT absorption peaks (Fig. 3a). Based on HRTEM and FT-IR spectroscopy, it can be concluded that $C_{61}(COOEt)_2$ **2** was inserted in SWNTs without decomposition, representing the first exohedral fullerene derivative to be encapsulated in a carbon nanotube.

After the same washing procedure as for **1** and **2**, $C_{61}(COOH)_2$ **3** was found to have preferentially formed a monolayer of fullerene on the outside of the SWNTs (Fig. 4). This effect is ascribed to the supramolecular aggregation of $C_{61}(COOH)_2$. Carboxylic groups in non-polar solvents (*i.e.* CO_2, CCl_4) readily form hydrogen bonds with COOH groups attached to other molecules, causing the aggregation of **3**. The effective size of the fullerene **3** functionalised with polar groups is significantly greater than the size of **1** or **2**. As a result the encapsulation of $C_{61}(COOH)_2$ in SWNTs is sterically prohibited. HRTEM demonstrates that dimeric structures $C_{61}(COOH)_2\cdots(HOOC)_2C_{61}$ formed *via* hydrogen bonding are very abundant on SWNT surfaces (Fig. 4 inset). The molecules of **3** were found to be noncovalently bonded to the SWNTs, more likely interacting by van der Waals forces, as the monolayer coating was removed by extensive washing of the sample with MeOH. After washing, the interiors of the SWNTs were visible, showing encapsulation of **3** in less than 1% of the SWNTs. The inhibition of filling with **3** relative to **1** and **2** can be attributed to dimerization of the dicarboxylic acid groups. $C_{61}(COOH)_2$@SWNTs structures are less stable in an electron beam than C_{60} or $C_{61}(COOEt)_2$. The molecules of $C_{61}(COOH)_2$ inside nanotubes degrade rapidly, forming polymeric structures (Fig. 2c).

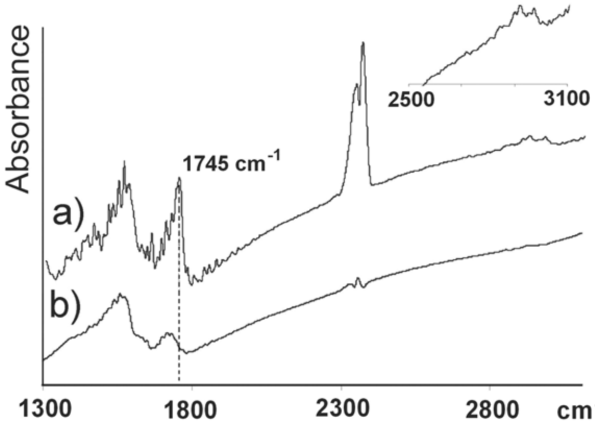

Fig. 3 FT-IR spectra of (a) $C_{61}(COOEt)_2$@SWNT (1745 cm^{-1} peak corresponds to C=O bond of ester groups; inset: magnified area of C–H vibrations) and (b) empty SWNTs.

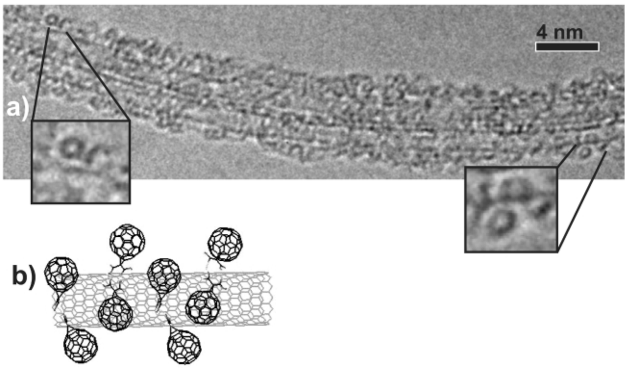

Fig. 4 (a) HRTEM micrograph showing two SWNTs covered with a layer of $C_{61}(COOH)_2$; insets show magnified areas. (b) Schematic diagram illustrating dimeric aggregates of $C_{61}(COOH)_2$ adsorbed on SWNT surface.

We have successfully encapsulated exohedrally functionalised fullerene cages inside carbon nanotubes for the first time. The method of SWNT filling in $scCO_2$ allowed the insertion of molecules bearing chemical functionalities at low temperature without affecting these functional groups. We have demonstrated that the host–guest interaction can be controlled by choosing suitable fullerene functional groups. Fullerenes with ester groups can enter SWNTs more easily than fullerenes with hydrogen bonding carboxylic groups. Rather, $C_{61}(COOH)_2$ preferentially coordinate to the SWNT exterior rather than forming peapods. The technique of filling nanotubes at low temperatures described herein opens the possibility of new forms of nanotube-based structures and, in turn, the potential to explore applications such as catalysis, molecular separation, and nanoscale drug delivery.[8]

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Notes and references

† HRTEM imaging was performed on JEOL4000CX electron microscope (information limit ~ 1.2 Å) at 100 kV accelerating voltage to minimise the knock-on damage. Typically 1 s exposures were used for imaging. Over 100 micrographs were taken from different areas of each specimen in order to estimate the SWNT filling factor. Specimens were found to be fairly homogeneous and the yield of 'peapods' was calculated by counting the number of filled nanotubes in each micrograph, and then averaging over the total number of micrographs taken for each specimen.

1 (*a*) B. W. Smith and D. E. Luzzi, *Chem. Phys. Lett.*, 2000, **321**, 169; (*b*) M. Monthioux, *Carbon*, 2002, **40**, 1890 and references therein.
2 B. W. Smith, D. E. Luzzi and Y. Achiba, *Chem. Phys. Lett.*, 2000, **331**, 137.
3 (*a*) H. Ulbricht, G. Moos and T. Hertel, *Phys. Rev. Lett.*, 2003, **90**, 95501; (*b*) S. Berber, Y. K. Kwon and D. Tomanek, *Phys. Rev. Lett.*, 2002, **88**, 185502; (*c*) L. A. Grifalco and M. Hodak, *Phys. Rev. B*, 2002, **65**, 125404.
4 (*a*) X. Camps and A. Hirsch, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1595; (*b*) C. Bingel, *Chem. Ber.*, 1993, **126**, 1957.
5 I. W. Chiang, B. E. Brinson, A. Y. Huang, P. A. Willis, M. J. Bronikowski, J. L. Margrave, R. E. Smalley and R. H. Hauge, *J. Phys. Chem. B*, 2001, **105**, 8297.
6 M. A. McHugh and V. J. Krukonis, *Supercritical fluid extraction: principles and practice*, 2nd edn., Butterworth-Heinemann, Boston, 1994.
7 B. W. Smith and D. E. Luzzi, *J. Appl. Phys.*, 2001, **90**, 3509.
8 C. R. Martin and P. Kohli, *Nature Rev. Drug Disc.*, 2003, **2**, 29.