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Microwave-assisted sidewall functionalization of single-wall carbon nanotubes by Diels–Alder cycloaddition†

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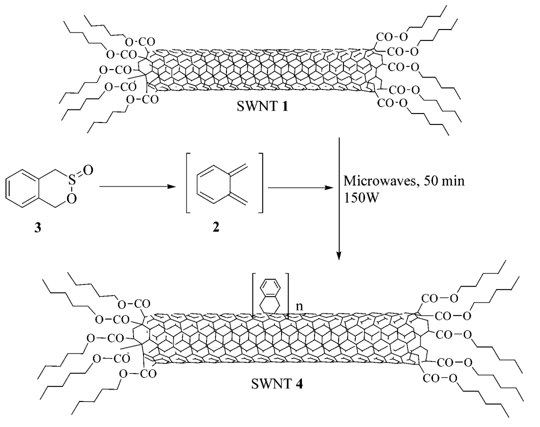
The first Diels–Alder cycloaddition of *o*-quinodimethane to SWNT has been performed under microwave irradiation.

The past decade has witnessed intensive theoretical and experimental efforts toward elucidating the physical properties of single-wall carbon nanotubes (SWNT).[1] Over the past few years, interest has focused on their chemical properties and their functionalization is actually a field of great interest.[2] Initially, attempts at functionalization were limited to oxidation reactions[3] to form shortened nanotubes with carboxylic acid groups on open edges. Haddon and co-workers first reported the use of these acid groups to attach long alkyl chains *via* amide linkages.[4] Later, Sun and co-workers showed that esterification can also be applied to functionalize SWNT.[5] More recently, reports have appeared on SWNT sidewall functionalizations using fluorine,[6] diazonium salts,[7] nitrenes,[8] organic radicals,[9] and azomethine ylides.[10] The Diels–Alder (DA) cycloaddition of *o*-quinodimethane onto the sidewalls of SWNT has been theoretically predicted to be viable due to the aromaticity stabilization of the transition state and product.[11] However, to the best of our knowledge, the plausibility of functionalizing the sidewalls of SWNT by means of DA cycloaddition has not been demonstrated.

[4+2] Cycloaddition reactions are among the most expeditious methods for the derivatization of fullerenes and selectively afford the adducts on 6,6-ring junctions. These systems can, in some cases, undergo a facile retro-Diels–Alder reaction as a consequence of the low thermodynamic stability of the resulting adduct.[12] Stable cycloadducts have, however, been prepared using different *o*-quinodimethanes.[13] In this communication, we report the first example of a DA cycloaddition to the sidewall of a SWNT.

DA functionalization was performed according to Scheme 1. Ester functionalized SWNT **1**[14] was reacted with *o*-quinodimethane (**2**),‡ generated *in situ* from 4,5-benzo-1,2-oxathiin-2-oxide (**3**) (sultine),[15] under microwave irradiation (a source of energy that has proven to be useful when applied in cycloaddition reactions[16] as well as in fullerene chemistry)[17] for 45 min. Work up of the reaction mixture gave modified SWNT **4**,§ thus providing an expeditious access to a new family of modified-SWNT. Finally, SWNT **4** was characterized by ^{1}H-NMR, UV-vis, FT-IR, FT-Raman spectroscopy as well as Surface Force Microscopy (SFM).



Scheme 1

The ^{1}H-NMR spectrum, which was recorded in CD_2Cl_2 (Fig. 1, lower spectrum) shows the peaks belonging to phenyl protons at $\delta = 7.6$ ppm; the peaks belonging to the methylene groups are found at around $\delta = 4.4$ ppm as very broad signals resembling the spectrum of the corresponding fullerene adduct 5[18] (Fig. 1, upper spectrum). The signal for the methylene group of the cyclohexene ring is very broad as a consequence of the restricted conformational inversion of the ring, a situation that also occurs in analogous fullerene derivatives.[19] The signals at δ = 3.0–3.8, 1.6, 1.3 and 0.9 ppm show the linking of the *n*-pentyl units to the SWNT.

FT-IR spectroscopy was also used to characterize the functionalized SWNT material **4**. The spectrum of SWNT **4** clearly indicates significant C–H stretching at *ca.* 2920 cm^{-1} due to the alkyl chains; above 3000 cm^{-1} a weak stretching for sp^2 hybridized C–H bonds in aromatic rings is observed (absent in the SWNT **1**). The stretching vibration of the C=O group is observed at 1720 cm^{-1} and the band at 1590 cm^{-1} is assigned to phenyl ring stretching. The UV spectrum of SWNT **4**, in dichloromethane, is the sum of the precursor ester-SWNT **1** and sultine **3**, with a maximum at 233 nm.

Preliminary characterization using a Surface Force Microscope in air at room temperature was performed on SWNT **1** and SWNT **4**. A dilution of 1 mg of material in 1 mL of dichloromethane (99.9% purity) was prepared and sonication was not needed in either case to obtain a good solution, which was stable for days. The samples were prepared by drop casting the solution on a freshly cleaved graphite substrate and scanned with an SiN cantilever with a 15 nm width tip. Static contact and dynamic tapping modes were used to characterize the samples. A large number of nanotubes could be observed and SWNT **1** samples were used as a test to

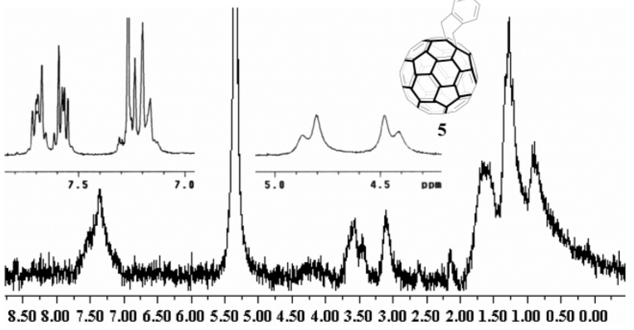


Fig. 1 1H-NMR spectra of SWNT **4** (recorded in CD_2Cl_2) (lower trace) and fullerene cycloadduct **5** (recorded in CDCl**3**) (upper trace).

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† Electronic supplementary information (ESI) available: Raman spectra of SWNT **1** and SWNT **4**. See http://www.rsc.org/suppdata/cc/b4/b402375g/

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confirm the average diameter of 2 nm and length of 1.8 microns with a more or less Gaussian distribution of lengths.

A brief summary of SFM results is shown in Fig. 2 for SWNT **4**. The XY in-plane scale is convoluted with tip width, so the nanotube diameter appears wider than it actually is, while in the perpendicular Z direction, the resolution shows real topographic height. The nanotube diameter is measured in the Z direction. The graph on the right shows three profiles along the lines A, B and C, respectively, marked on the images. Two different nanotubes are shown, both of which show the main result of this topographic characterization: diameters along lines B and C (and C*, not shown for the shake of clarity) have the expected diameter of 2 nm, the same as that obtained for all the SWNT **1** samples, but at some points (A and A*) a clear increase in height of about 1 to 1.5 nm is observed. We believe that these bumps are a clear indication of the points at which the nanotubes have been functionalized by the DA cycloaddition of *o*-quinodimethane. It is likely that the cycloaddition occurs in nanotube zones in which the density of pentagon–heptagon defects in the nanotube lattice is higher, thus providing the cycloaddition of various groups in the same area. We expect that the correlation between defect density and functionalization could be demonstrated with atomic resolution SFM measurements in an ultra-high vacuum.

The Raman spectrum of SWNT **1** shows two peaks, one at 1636 cm^{-1} ascribed to the carboxylate groups and another at 1596 cm^{-1} arising from the commonly observed tangential mode of SWNT (see Fig. 3 in Electronic Supplementary Information†).[20] After treatment of SWNT **1** the frequency of the tangential mode downshifts to 1590 cm^{-1} as a consequence of the effective side functionalization in SWNT **4**. Furthermore, the bands at around 1290 cm^{-1} in SWNT **4** are relatively enhanced with respect to that in SWNT **1**, a fact that provides further evidence of the covalent link to the sidewall nanotube.

In summary, we have demonstrated the viability of the theoretically predicted Diels–Alder cycloaddition of *o*-quinodimethane onto the sidewall of a SWNT by using microwave irradiation. This process offers a new and powerful methodology to functionalized carbon nanotubes. This result opens a new possibility to obtain SWNT with better solubility for technological applications.

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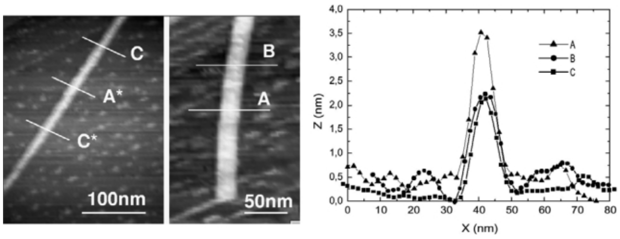

Fig. 2 Topographic SFM images of two different SWNT **4** on a graphite substrate, the Z-profiles indicated with lines A, B, and C are shown in the graph at the right. Diameters of 2 nm are measured, in some points bumps of 1.5 nm are an indication of DA cycloaddition of *o*-quinodimethane to the nanotubes.

Notes and references

‡ The synthesis of SWNT **4** was achieved by mixing 150 mg (0.9 mmol) of **3** and 20 mg of ester functionalized SWNT **1** in 40 mL of *o*-dichlorobenzene (ODCB). The mixture was irradiated in a focused microwave reactor[21] at 150 W for 45 min. The ODCB was removed by vacuum distillation and the residue was purified by washing several times with pentane and diethyl ether to obtain SWNT **4** (15 mg) as a dark brown solid. SWNT **4** is soluble in chloroform, dichloromethane and tetrachloroethane, less soluble in methanol, acetone and THF, and is not soluble in pentane or diethyl ether.

§ The reaction was performed by classical heating for 72 h in refluxing ODCB; nevertheless, the ^{1}H-NMR spectrum shows only a low degree of conversion.

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