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Synthesis of dendrimer–carbon nanotube conjugates

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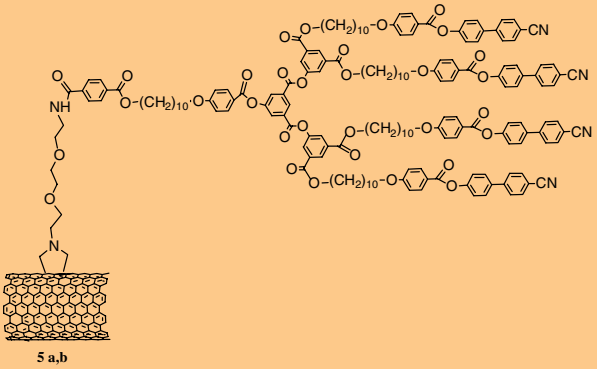
We describe the coupling between Carbon Nanotubes (CNTs) and a second-generation cyanophenyl-based dendrimer. The goal of our work is the synthesis of highly functionalized CNTs without provoking damage to the conjugated π-system. One approach is the attachment of dendrimers with a high density of functional groups to the CNTs. These groups serve as anchor points for further reactions. With this aim, we have carried out a primary modification on CNTs by the use of 1,3 dipolar cycloaddition reaction. We have employed Single Wall Carbon Nanotubes (SWNTs) as well as Multi Wall Carbon Nanotubes (MWNTs) obtaining 238 μmol and 511 μmol of pyrrolidine groups per gram, respectively. The amount of amino groups introduced in the system was measured by the Kaiser test as well as thermogravimetric analyses. As a second step, dendrimer incorporation was performed by carbodiimide chemistry. Thermogravimetric Analysis, Raman Spectroscopy and Atomic Force Microscopy characterization techniques are reported for the characterization of the final CNT–dendrimer conjugate. The results show that the dendrimer has been attached covalently to the previously generated amine groups. Morphologically, the attached dendrimer with an estimated theoretical molecular length of 6.4 nm, generates a wrapping of 8 nm thick around the CNTs walls.



Scheme of the synthesized CNT–dendrimer conjugate.

1 Introduction Since Carbon Nanotubes (CNTs) were discovered in 1991 by Ijima et al. [1], a great interest has been developed from a fundamental point of view and for potential applications [2]. However, the lack of solubility and the difficult manipulation in any solvents have imposed great limitations to the use of CNTs. Several research groups are currently engaged in the chemical modification of CNTs [3–5]. Unfortunately, surface modification of these nanomaterials involves a change in their properties such as the π-conjugation of the system. For this reason, the researchers are aimed at the synthesis of new highly functionalised CNTs whose physical properties remain unaltered after chemical modification [6].

We have developed a 1,3 dipolar cycloadition reaction of azomethine ylides generated in-situ by thermal condensation of aldehydes and α-amino acids [7, 8]. This reaction gives rise of soluble CNTs due to the high number of pyrrolidine moieties attached at the CNTs sidewalls. Addition of nitrenes [9] and carbenes [10–12] or aryl radicals generated by electrochemical reduction of the diazonium salts [13] are other examples of addition reactions at CNTs sidewalls.

The attachment of macromolecules at CNTs such as polymers or dendrimers is another strategy used to improve the solubility of these nanomaterials. While many studies are developed for the attachment of polymers at CNTs [14], the decoration of CNTs sidewalls with dendrimers is an emerging area [15–19].

Dendrimers, a unique class of polymers, are highly branched macromolecules, whose size and shape can be precisely controlled. The well-defined structure, a monodisperse size distribution, surface functionalization capability, and stability are properties of dendrimers that make them attractive drug carrier candidates [20].

The synthesis of the second-generation dendrimer used in the present work is reported in previous works [21–23]. The procedure is based on the condensation of the phenol based dendrimer to give the corresponding aldehyde derivative and a final oxidation to carboxylic terminal second generation cyanobiphenyl-based dendrimer with liquid crystalline promoter property. Applying the 1,3 dipolar cycloaddition reaction, this synthesized dendrimer was attached at fulleropyrrolidines.

Our study focuses on the preparation of CNT-dendrimer conjugates. We have obtained CNTs with high amount of pyrrolidine moieties by means of 1,3 dipolar cycloaddition reaction. The amino terminal groups of the attached functionalities serve as anchor point to obtain CNTs-dendrimer conjugates. We show the versatility of the proposed mechanism that serves for both types of CNTs: (Single Wall Carbon Nanotubes) SWNTs and (Multi Wall Carbon Nanotubes) MWNTs. The final highly hyperbranched CNT products possess a high number of terminal functional groups for further interesting attachments without damaging the CNTs network.

2 Experimental

2.1 Materials and equipments HiPCO Single Wall Carbon Nanotubes (SWNTs) were purchased from Carbon Nanotechnologies Incorporated, CNI® and were purified for further reactions. Multi Wall Carbon Nanotubes (MWNTs), 20–40 nm diameter, were purchased from NanoAmor, Nanostructured and Amorphous Materials, Inc. and used as received. All the reagents were used as purchased from Sigma-Aldrich.

The thermogravimetric analyses were performed with a TGA Q500 TA Instruments at 10 °C/min under N_2.

Raman experiments were performed in a RENISHAW In Via Raman Microscope. The laser light wavelength was 785 nm.

For the TEM analyses a small amount of nanotubes was dissolved in DMF and a drop of the solution was placed on Cu grids or lacey carbon grids. After drying, the sample was investigated with a Philips EM 208 with an accelerating voltage of 100 kV.

For the AFM analyses, a small amount of nanotubes was dissolved in DMF and a drop of the solution was placed on a freshly cleaved mica slide. After drying, the sample was investigated with a MultiMode™ Atomic Force Microscope from Digital Instruments.

2.2 Experimental procedure

2.2.1 1,3-dipolar cycloaddition and amino acid deprotection SWNTs (100 mg) were purified by 2.6 M nitric acid treatment (100 ml) stirring overnight at 120 °C. After this treatment, the nanotubes were separated from the residue by filtration over a Millipore membrane (GTTP 0.2 μm) and extensively washed with water and dried. In two round-bottom flasks purified SWNTs (**1a**) (50 mg) and pristine MWNTs (**1b**) (50 mg) were suspended in DMF (100 ml) adding paraformaldehyde and a previously synthesized amino acid derivative [24] in portions (100 mg of each compound every 24 h). The mixture was refluxed 5 days at 115 °C with sonication of 10 min after each addition. At the end of the reaction, the suspension was centrifuged and the supernatant was set aside. Fresh DMF was added to the black solid and sonicated-centrifuged until the supernatant solution remained colourless. All the supernatant solutions were collected together. Functionalized SWNTs (**2a**) and MWNTs (**2b**) (see Fig. 1), were recovered from the supernatant by filtration over a Millipore employing 0.22 μm fluoropore membrane, extensively washed with dimethylformamide (DMF), dichloromethane (DCM) and diethylether (Et_2O) and dried under high vacuum. Modified SWNTs (**2a**) and MWNTs (**2b**) (10 mg) were suspended in anhydrous DMF (20 ml) and the Boc protecting group was removed by bubbling gaseous HCl through the suspension. The mixture was stirred during 1 hour at room temperature under inert atmosphere. The corresponding ammonium chloride salts **3a** and **3b** precipi-

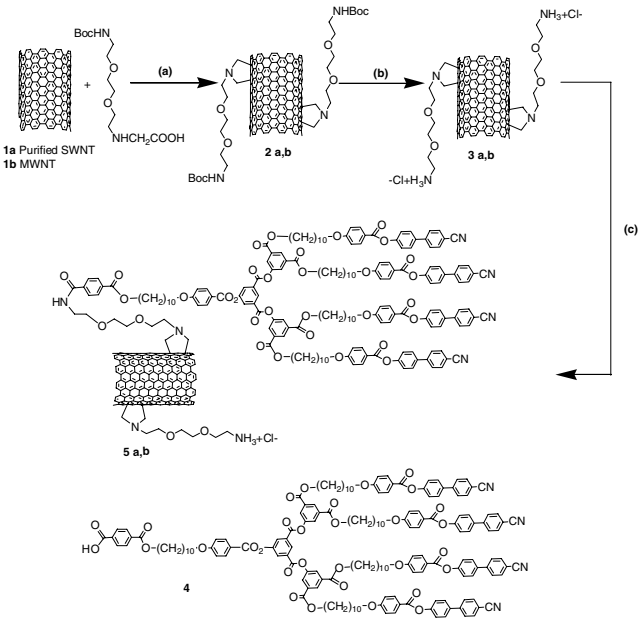


Figure 1 Reagents and conditions: (a) paraformaldehyde, DMF, 115 °C, 5 days; (b) gaseous HCl, DMF, RT, 1 h; (c) EDC, HOBt, Et_3N, dendrimer **4**, CH_2Cl_2, RT, 12 h.

tated during the acid treatment were recovered by vacuum filtration over a Millipore 0.22 µm fluoropore membrane and extensively washed with DMF, DCM and Et_2O and dried under high vacuum.

2.2.2 Synthesis of the dendrimer–CNT derivatives The dendrimer coupling was performed employing 6 mg and 2.5 mg of functionalized SWNTs (**3a**) and MWNTs (**3b**), respectively. These values correspond to 1.3 µmol of amino groups based on the loading calculated with the quantitative Kaiser test. In both cases, dendrimer **4** (11 mg, 4 µmol) in distilled DCM (15 ml) was added. N-[3-(dimethylamino)propyl]-N-ethylcarbodiimide (EDC, 0.5 mg, 2.6 µmol), hydroxybenzotriazole (HOBt, 0.35 mg, 2.6 µmol) and anhydrous triethylamine (1 ml) were added as coupling agents. The mixture was stirred 12 h under inert atmosphere at RT. The product was recovered by vacuum filtration over a Millipore 0.22 µm fluoropore membrane and extensively washed with DMF, DCM and Et_2O and dried under high vacuum.

3 Results and discussion The well-known cycloaddition reaction was performed on the purified SWNTs and on the MWNTs. Once we obtained the amino group free by the deprotection of the *N*-Boc group, the dendrimer was attached by a simple coupling at room temperature. All the synthesized products were characterized.

3.1 Thermogravimetric analysis (TGA) The amount of functional groups in the functionalized nanotubes was determined by TGA. It is calculated by the correlation between the loss of weight at the degradation temperature of the attached functional groups to the CNTs and their molecular weight. Compounds **2** and **5** have been characterized as SWNT as well as MWNT derivatives. Consequently, the yield of coupling reaction between the dendrimer and the CNT can be estimated comparing the functional groups concentration in the two compounds **2** and **5**.

Table 1 summarizes the obtained results. The loss of weight of compound **2** at 500 °C and compound **5** at 800 °C in both, MWNTs and SWNTs was calculated. In the case of the MWNTs (see Fig. 2), the starting pristine MWNTs (**1b**) did not present any loss of weight at these temperatures hence the loss percentage can be assigned directly to the organic functionalities. In compound **2b** there is one pyrrolidine moiety per 140 C atoms, which means,

Table 1 Thermogravimetric results.

	compound	loss of weight (%)	µmol/g	reaction (c) yield (%)
MWNT	**2b**	$14_{T=500\,°C}$	511	24
	5b	$34_{T=800\,°C}$	116	
SWNT	**2a**	$19_{T=500\,°C}$	238	18
	5a	$36_{T=800\,°C}$	42	

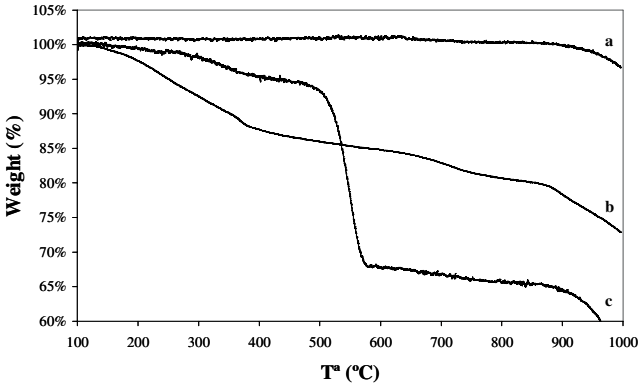


Figure 2 TGA of pristine MWNT **1b** (a), functionalized **2b** (b) and **5b** (c).

511 µmol of pyrrolidine groups/g. In compound **5b** one dendrimer molecule per 472 C atoms can be calculated. This corresponds to 116 µmol of dendrimer/g. Consequently, nearly 24% of the amines present on the compound **3b** have reacted with the dendrimer in the reaction (c) of Fig. 1.

In the case of SWNTs, the loss of weight of the starting purified SWNTs (**1a**) at 500 °C and at 800 °C is 14% and 27%, respectively (see Fig. 3). Taking into account the obtained percentages, an easy correlation gives one pyrrolidine group per 327 C atoms in compound **2a**, which means, 238 µmol of pyrrolidine groups/g. In the same way, the calculations establish one dendrimer molecule per 1732 C atoms in compound **5a** giving about 42 µmol of dendrimer/g. Then the dendrimer is covalently attached to 18% of the amines present in compound **3a**. Either on the 1,3 dipolar cycloaddition or the consequent attachment of the dendrimer, the reactivity of the MWNTs is shown to be higher than on SWNTs. This fact could be due to the better dispersion of the MWNTs in the reaction medium enhancing the contact of the nanotubes reactive sites with the reacting molecules and the presence of a higher number of defects.

3.2 Kaiser test The Kaiser test [25, 26] is a useful tool to quantify the amount of amino terminal groups of deprotected CNT derivatives **3**. In the case of MWNTs de-

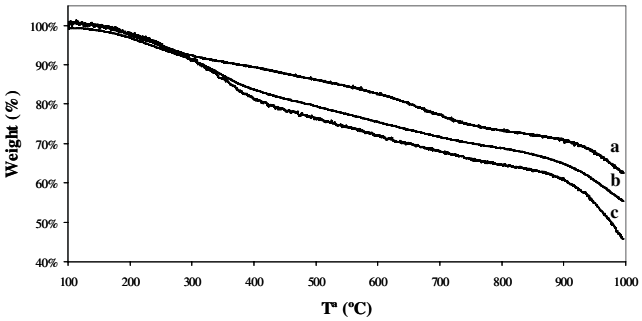


Figure 3 TGA of purified SWNT **1a** (a), functionalized **2a** (b) and **5a** (c).

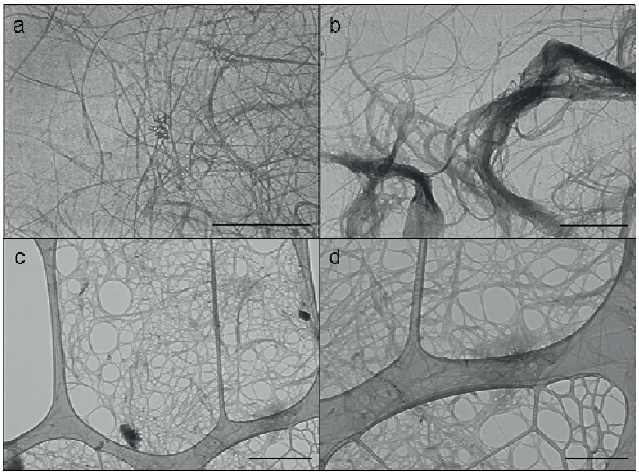


Figure 4 TEM images of SWNT derivative **2a** (a), the non functionalized SWNT separated as by product (b) both of them obtained employing Cu grids and SWNT derivative **5a** (c and d) obtained employing lacey carbon grids. Scale bars: (a) and (b) 500 nm, (c) and (d) 1000 nm.

rivative **3b**, we found an amine loading of 518 μmol/g. On SWNTs derivative **3a**, the amine loading is 210 μmol/g. These results are in excellent agreement with the TGA.

3.3 Microscopy characterization We have characterized SWNTs derivative **2a** by Transmission Electron Microscopy (TEM). As explained in the experimental procedure, we have separated the functionalized CNTs from the non-functionalized ones after the 1,3 dipolar cycloaddition reaction. TEM is a useful tool to qualitatively analyze both samples and to study morphological differences. In fact, as the images of Fig. 4 show, the functionalized SWNTs **2a** have a higher degree of purity and dispersability compared with the separated non-functionalized CNTs. In Fig. 4 TEM images of the derivative **5a** can also be observed. In this case the SWNTs are supported on lacey carbon films.

3.4 Atomic force microscopy The diameter of the samples corresponding to compounds **2a** and **5a** in SWNTs were measured by Atomic Force Microscopy (AFM). The analysis of 49 nanotubes in the sample corresponding to compound **2a** resulted on a diameter distribution in the range of 2–4 nm. In the case of compound **5a**, the average diameter gives 10–12 nm on a statistics of 42 nanotubes. According to these measurements, covalently attached dendrimer generates a wrapping of 8 nm thick around the SWNTs. In a previous work [21] the molecular length of the dendrimer was estimated for the fully extended conformation obtained by means of HyperChem software. This value corresponds to 6.4 nm. Hence, the obtained dendrimer wrapping is a slightly small than the theoretical prediction.

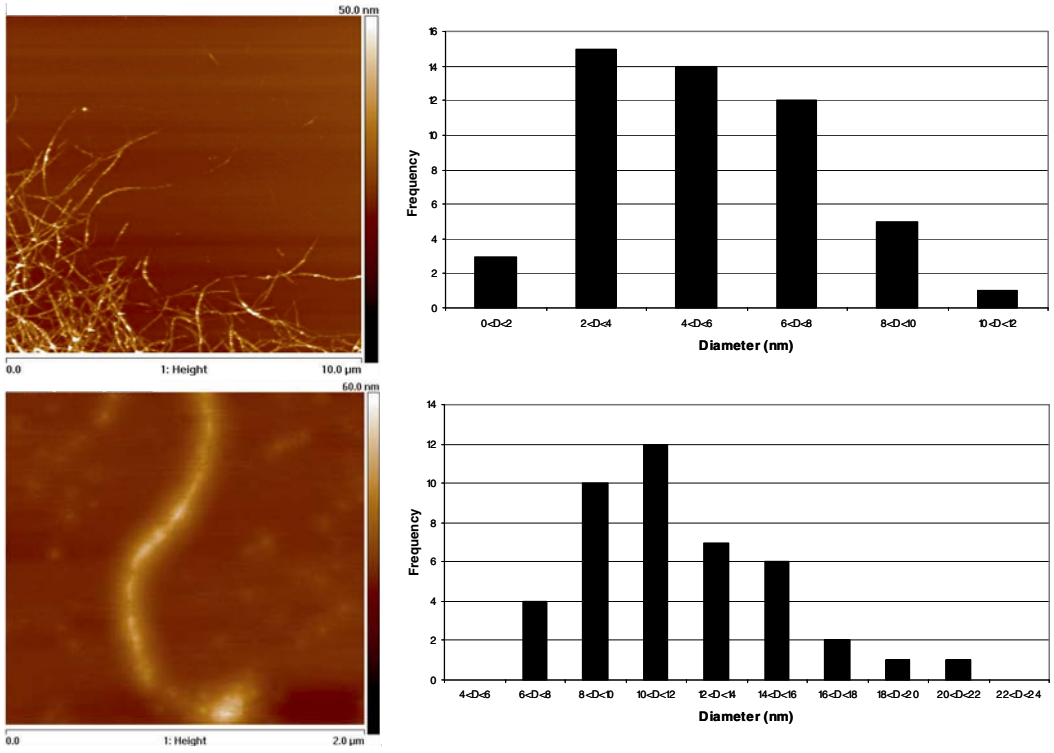


Figure 5 (online colour at: www.pss-a.com) AFM image of compound **2a** and diameter distribution of the sample (top) and that of the compound **5a** (botton).

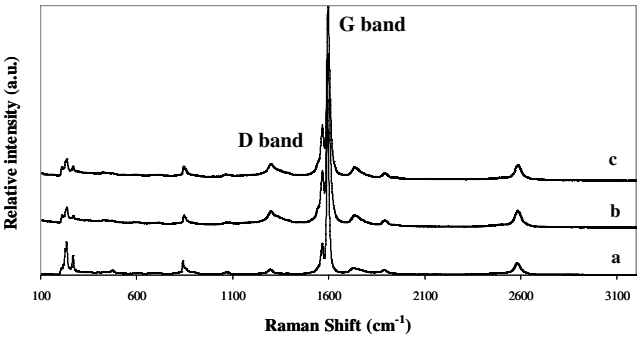


Figure 6 Raman spectra of pristine SWNT (a), compound **2a** (b) and compound **5a** (c) of modified SWNTs.

3.5 Raman spectroscopy Raman Spectroscopy is a valuable characterization method of CNTs because it provides information about the structure and properties [27]. Figure 6 shows the Raman spectra of derivatives **2a** and **5a** in comparison with the Raman spectra of pristine SWNTs. In all cases, three important features of SWNTs can be observed, the tangential G-band (at 1595 cm^{-1}) which is derived from the in-plane Raman active mode in graphite, the disorder-induced D-band (at 1290 cm^{-1}) and the Radial Breathing Mode (RBM) peaks at low Raman shifts. Changes in the D-band can be used for materials characterization to probe and monitor structural modifications of the nanotubes sidewalls that come for the increment on the carbon sp^3 due to the attachment of different chemical species. The D/G intensity ratio in pristine SWNTs is 2.6%. However in compounds **2a** and **5a** the D/G intensity relation increases and in both cases is 8.9%. As expected, the D-band intensity is lower in the pristine SWNTs compared to the functionalized SWNTs (**2a**, **5a**). The functionalization increases, the sp^3 hybridization in the SWNT lattice and consequently the disorder induced D-band intensity. Nevertheless, the D/G intensity relation on compound **2a** and compound **5a** has the same value. This means that the dendrimer is attached to amino terminal groups and no further reactions on the SWNTs sidewalls take place, therefore non-specific adsorption is ruled out. Furthermore, the low increase of D/G intensity relation comparing with the pristine SWNTs demonstrates a low degree of functionalization.

4 Conclusions We have described the covalent attachment between Carbon Nanotubes (CNTs) and a second-generation cyanobiphenyl-based dendrimer with both types of CNTs: SWNTs and MWNTs. 1,3 dipolar cycloaddition reaction was employed as a primary modification of the CNTs sidewalls. The pyrrolidine functional group concentration has been estimated in SWNTs and MWNTs after the reaction with two different methods: Thermogravimetric Analysis and Kaiser quantitative test. Both of them confirm a pyrrolidine concentration of 238 μmol/g and 511 μmol/g in SWNTs and MWNTs, respectively. The dendrimer attachment at the deprotected amino terminal groups of modified CNTs has been carried out by carbodiimide chemistry. Also in this coupling reaction, a higher reaction yield on MWNTs with respect to SWNTs has been demonstrated. In the former, 24% of the amines reacted with the dendrimer and in the latter, 18% of the amines. Moreover, Raman Spectroscopy confirms the attachment of the dendrimer to the amine groups on SWNTs instead of the direct reaction with the SWNTs lattice. This covalently attached dendrimer (molecular length of 6.4 nm) is wrapped around the SWNTs with a thickness around 8 nm. The high density of anchor points in comparison with the low damage caused in the conjugated π system on CNTs makes the conjugate very interesting for further applications. Besides, we have demonstrated the versatility of the proposed mechanism since it works with both, MWNTs and SWNTs.

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