

# Dendrimers and nanotubes: a fruitful association

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Dendrimers and nanotubes (particularly carbon nanotubes (CNTs)) are two types of nano-objects which have met independently a large success within the scientific community. Surprisingly, their association has been poorly studied up to now, despite some original properties recently reported and that will be emphasized in this *tutorial review*. One can name as a few, the elaboration of single-walled carbon nanotubes from dendrimers, CNTs functionalised with dendrimers displaying field effect transistor properties and/or used as biosensors, and modified biological properties (either enhanced biocompatibility or enhanced antimicrobial activity). However, not all the nanotubes are carbon nanotubes, and original properties were also reported for dendrimers associated with non-CNTs, such as the elaboration of specific nano-filters and of highly efficient and reusable catalysts. Furthermore, non-CNTs constituted of dendrimers, particularly those obtained by layer-by-layer deposition of positively and negatively charged dendrimers associated with quantum dots display an excellent detection limit for DNA hybridization (10 fM).

## Introduction

“Nanotechnology is the creation of useful materials, devices, and systems through the control of matter on the nanometre-length scale, and the exploitation of novel properties and phenomena developed at that scale”.<sup>1</sup> This definition proposed by the Interagency Working Group on Nanosciences, Engineering and Technology constitutes the general background of this review, which will emphasize all aspects, including the potential uses, of the combination between two

“hot” topics of nanotechnologies: dendrimers and nanotubes. The very first example of such a combination is recent, since it dates back to 2001, and most papers were published in the past five years. This fact emphasizes the novelty of this field of research, and the fact that there is still plenty of room to continue this pioneering work.

Dendrimers<sup>2</sup> are a very special type of polymer since, despite being constituted by the association of branched repetitive units, they are never synthesized by polymerization reactions, but step-by-step, generally radially from a central core. Each level of branching units creates a new generation. Such a method of synthesis ensures a control over the whole architecture, a nanometric size, and a high level of mono-dispersity, unlike all other types of polymers. Most of the

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preparation and properties of dendrimers and hyperbranched polymers with emphasis on their applications in different fields ranging from biology, nanomaterials and catalysis. He is a member of several Academies of Science worldwide. He is author of around 450 publications and 39 patents.

properties of dendrimers are related to the nature of their numerous terminal groups that may be varied at will to fulfil the desired properties.

“Nanotubes” is a word that is completed very often by “carbon”. Indeed, carbon nanotubes are allotropes of carbon with a cylindrical structure that are useful in many aspects of nanotechnologies. Two categories of carbon nanotubes are known. The multi-walled carbon nanotubes (MWCNTs)<sup>3</sup> were the first discovered; they are made of concentric cylinders placed around a common central hollow. The single-walled carbon nanotubes (SWCNTs)<sup>4</sup> have a single-layer cylinder extending from end to end, and possess a good uniformity in diameter (1–2 nm).<sup>5</sup> Carbon nanotubes will constitute an important part of this paper, but other types of nanotubes made of polymers interacting with dendrimers or even nanotubes exclusively constituted of dendrimers will be also considered.

This tutorial review is not a fully comprehensive review, but it will highlight the most important aspects of this new field of research.

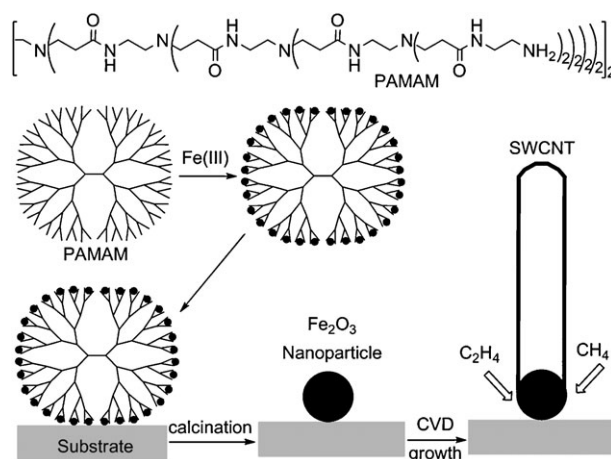
## Dendrimers and carbon nanotubes

Most of the publications in this field deal with the functionalisation of carbon nanotubes with dendrimers or dendrons (a dendron is a dendritic wedge, having one functional group at the core, and several functional terminal groups). These functionalisations can be either covalent or non-covalent, and employ generally poly(amidoamine) (PAMAM)<sup>2a</sup> dendrimers or dendrons. This association has led to applications and uses in various fields concerning the obtaining of nanoparticles, the elaboration of (bio)sensors, and biology. However, there also exists some papers concerning the use of dendrimers to obtain carbon nanotubes, as will be emphasized in the next paragraph.

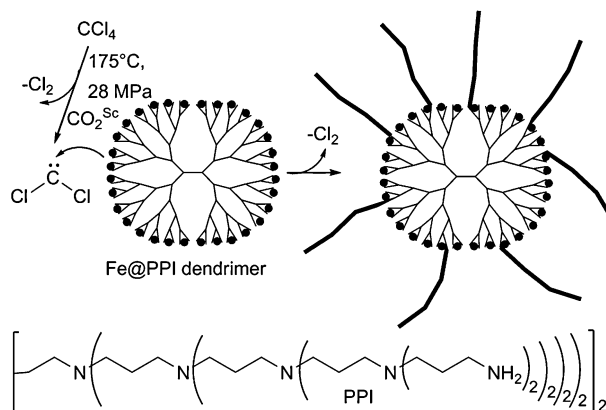
### Carbon nanotubes elaborated with dendrimers

In all cases, the dendrimers are used to elaborate first metallic nanoparticles (NPs), which then are used as catalysts to generate the carbon nanotubes at high temperature. The majority of nanoparticles generated for this purpose are iron NPs, more precisely  $\text{Fe}_2\text{O}_3$  NPs. This concept is illustrated on Scheme 1. A high generation ( $G_4$  or  $G_6$ ) PAMAM dendrimer was reacted with  $\text{Fe(III)}$  (generally  $\text{FeCl}_3$ ) and the mixture was calcinated to afford nearly monodisperse  $\text{Fe}_2\text{O}_3$  NPs, thanks to the dendrimers acting as templates. Using the chemical vapour deposition (CVD) technique (a classical technique for the synthesis of CNTs) at  $900^\circ\text{C}$  with  $\text{CH}_4/\text{C}_2\text{H}_4$  as carbon source induced the synthesis of SWCNTs,  $\text{Fe}_2\text{O}_3$  NPs being the catalyst.<sup>6</sup> The same type of concept was also applied with a poly(propyleneimine) (PPI) dendrimer-based  $\text{Co}_{32}$  nanocluster (using  $\text{CH}_4/850^\circ\text{C}$ ),<sup>7</sup> and with a PAMAM dendrimer reacted with  $\text{NiCl}_2$  (using  $\text{C}_2\text{H}_2/650^\circ\text{C}$ ).<sup>8</sup> Microwave plasma-enhanced CVD with  $\text{Fe}_2\text{O}_3$  NPs was used for lowering the temperature to  $400^\circ\text{C}$ , or obtaining MWCNTs.<sup>9</sup>

In order to keep the dendrimers in the reaction media and to take profit of their presence to elaborate the CNTs, the



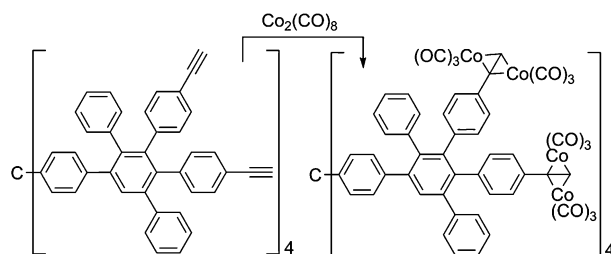
**Scheme 1** Synthesis of carbon nanotubes from iron nanoparticles obtained by calcination of PAMAM dendrimer complexes.



**Scheme 2** Carbon nanotubes elaborated from iron-PPI dendrimers in mild conditions (supercritical  $\text{CO}_2$ ).

temperature could be still lowered. Using a “wet technique” (in solution), iron-encapsulated PPI dendrimers afforded MWCNTs at lower temperature ( $175^\circ\text{C}$ ) via the decomposition of  $\text{CCl}_4$  in supercritical  $\text{CO}_2$  (Scheme 2).<sup>10</sup>

Another original concept was derived from the cobalt complexes of polyphenylene dendrimers (Scheme 3). Their pyrolysis at  $600\text{--}800^\circ\text{C}$  afforded carbon/Co nanorods, from which CNTs were grown. In these cases, the dendrimer complexes acted both as precursor of the catalysts and as source of carbon. Using tetraphenylmethane as an additional source of carbon afforded and increased amount of CNTs.<sup>11</sup>



**Scheme 3** Cobalt complex of a polyphenylene dendrimer, used both as catalyst and as carbon source for the elaboration of CNTs.

## Association of carbon nanotubes by dendrimers

The very first example of interaction between nanotubes and dendrimers produced stars, elaborated from the covalent reaction between the tenth generation PAMAM dendrimers and SWCNTs derivatized with acid chloride groups. Due to the higher reactivity of the acid chlorides located at the open ends compared to those at the side wall, only the ends of SWCNTs reacted with dendrimers terminal groups to produce star-shaped objects, as shown by atomic force microscopy (AFM).<sup>12</sup>

In order to obtain topologically stable and morphologically static three-dimensional assemblies of SWCNTs, molecular systems that are similar in size to the diameter of the SWCNTs are required. A supramolecular dendritic complex synthesized from enantiomerically pure  $[\text{Ru}(\text{diimine})_3]^{2+}$  units have led in particular to the  $[\Lambda_6\Delta_3\Lambda\text{-Ru}_{10}]^{20+} [\text{PF}_6^-]_{20}$  metallodendrimer, which is planar with a diameter of 5.8 nm and a thickness of 0.9 nm, highly symmetrical, and rigid. SWCNTs can bind by physisorption to the endoreceptors as shown in Fig. 1, but binding to the exoreceptors can also be envisaged, in particular for larger SWCNTs.<sup>13</sup> It was shown that the metallodendrimers bind strongly and specifically to the ends of the SWCNTs. Very recently, it was shown that the SWCNTs bound to these metallodendrimers have a narrow diameter range of  $0.84 \pm 0.03$  nm, a value which is consistent with the docking to the endoreceptors.

Additionally, these supramolecular complexes exhibit spectroscopic effects consistent with charge (electron) transfer from the metal centre through the ligand and finally onto the SWCNTs. Such property was found useful to fabricate field effect transistors (FET).<sup>14</sup> It must be emphasized that FET devices elaborated with CNTs have generated a large number of sensors for the detection of both chemical and biological species, which possess an extreme environmental sensitivity,

small size and ultra-low power requirements.<sup>15</sup> Some examples concerning the use of dendrimers-CNTs to elaborate FETs will be given throughout this review.

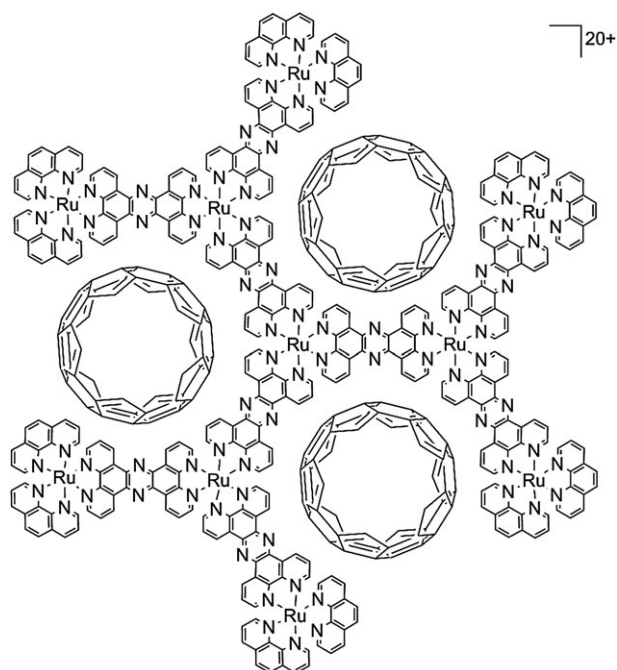
## Covalent functionalisation of carbon nanotubes with dendrons

SWCNTs mostly exist in bundles due to strong intermolecular cohesive forces between tubes, resulting in poor solubility in all solvents. Thus, functionalisation is an important tool for the full exploitation of SWCNTs properties,<sup>16</sup> and dendrimers appear as an attractive alternative to classical organic functionalisations.

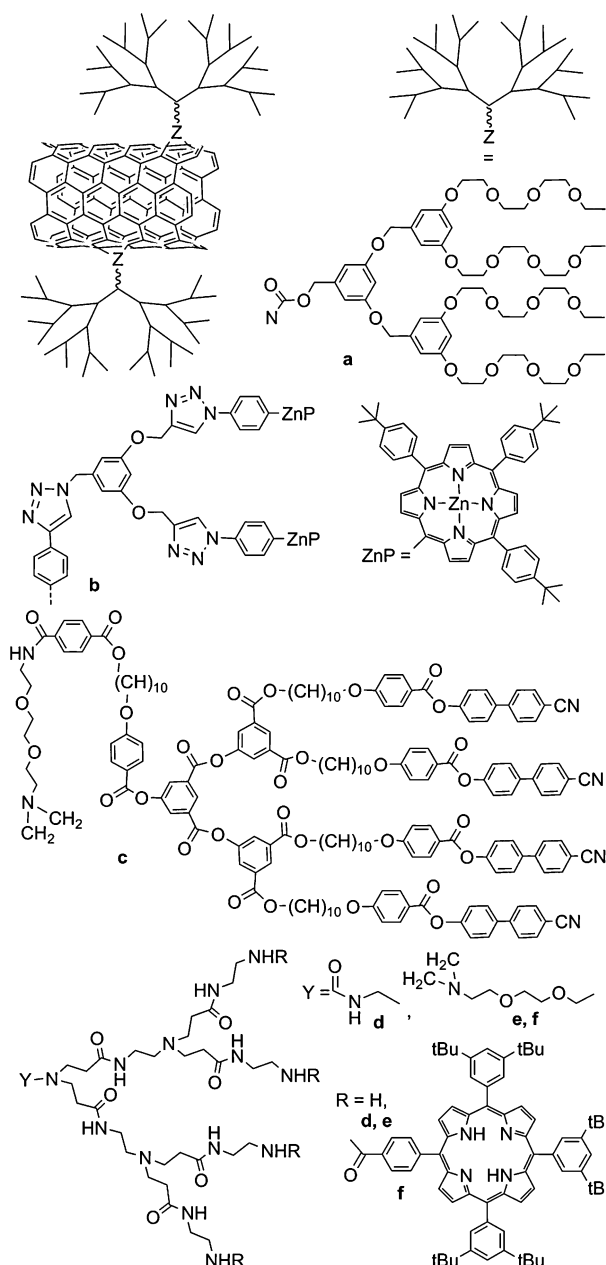
Several types of dendrons were either grafted or built onto SWCNTs. In the first example, a small dendron having oligoethyleneglycol (OEG) terminal groups and an azido-carbonate core was used for the sidewall functionalisation of SWCNTs (case **a** in Fig. 2). In this case, the functionalisation occurs *via* nitrene addition across a double bond of the SWCNT. Such a functionalisation increased the solubility in DMSO, but a smaller compound (2 OEGs instead of 4) increased more the solubility in a variety of solvents.<sup>17</sup> Another azide was recently used to graft Zn porphyrin (ZnP) dendrons to SWCNTs *via* “click” chemistry on the triple of SWCNTs pre-functionalized with ethynyl aniline (case **b** in Fig. 2). Upon selective photoexcitation of ZnP, the formation of reduced SWCNTs and oxidized ZnP was observed.<sup>18</sup> A second generation cyanobiphenyl-based dendron was also grafted onto pre-functionalised SWCNTs and MWCNTs. 1,3-dipolar cycloaddition reaction was employed as a primary modification, then the attachment of the dendron was carried out using carbodiimide chemistry (case **c** in Fig. 2).<sup>19</sup> Contrarily to the previous cases, PAMAM dendrons were not directly grafted but built step-by-step onto SWCNTs functionalised by amines (cases **d**, **e**, **f** in Fig. 2). Case **d** nanotubes were first functionalized with carboxylic acids (from  $\text{H}_2\text{SO}_4/\text{HNO}_3$ ) which were subsequently transformed to acyl chloride, then reacted with ethylenediamine. The dendron growth began from this point. The resulting functionalised SWCNTs display a high solubility in water.<sup>20</sup> In cases **e** and **f**, the SWCNTs were first functionalized with paraformaldehyde and a carbonate bearing a boc-protected amine. The terminal groups of case **e** were used for the grafting of tetraphenylporphyrin (TPP) moieties to afford case **f**. The excited-state interaction between the TPPs and the SWCNTs induced a quenching ( $\sim 85\%$ ) of the TPP fluorescence.<sup>21</sup>

## Non covalent functionalisation of carbon nanotubes with dendrimers or dendrons

Another way to suppress or diminish the aggregation of CNTs into bundles and ropes consists in using non-covalent interactions between various types of molecules and nanotubes. An important advantage of the non-covalent approach is that it should not create defects in the CNTs.<sup>22</sup> In order to favour these non-covalent interactions, hydrophobic functions such as conjugated aromatic groups appear as the most suitable. In particular, a PAMAM dendron bearing anthracene as core<sup>23</sup> and a generation 3 PAMAM dendrimer bearing naphthalene diimide terminal groups<sup>24</sup> were shown able to strongly interact with SWCNTs. A fullerene dendron was also used for the same purpose, inducing dispersion of the CNTs in THF<sup>25</sup> (Fig. 3).

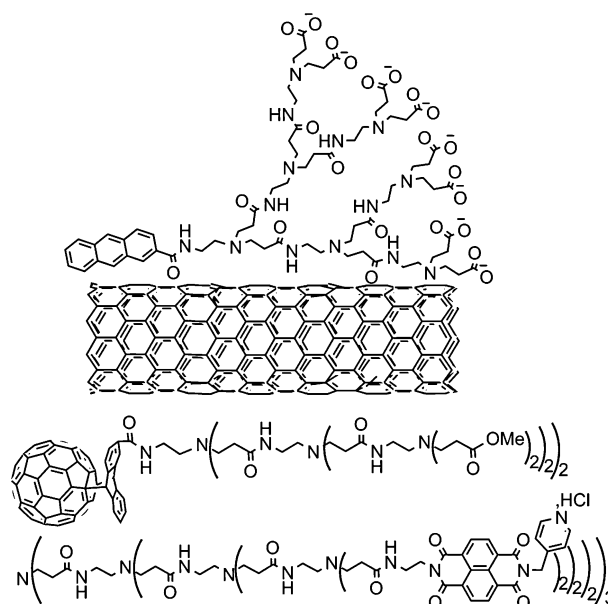


**Fig. 1** “Mechanically” docked metallodendrimers about single-walled carbon nanotubes.



**Fig. 2** Types of dendrons covalently linked to single-walled carbon nanotubes (cases **a–c**) or built on it (cases **d–f**).

In the case of the anthracene dendron, light-induced electron transfer, electron migration, and hole-shift processes of SWCNT-anthracene dendron were observed in the presence of methylviologen dication ( $MV^{2+}$ ) as an electron mediator and electron pool, and 1-benzyl-1,4-dihydronicotinamide (BNAH) as a hole shifter. In the case of CNTs coated with the electrical conducting dendrimer (PAMAM-naphthalene diimide), field-effect transistor (FET) device collectively exhibits large electrical conductance changes under electrostatic gating, owing to the interaction between SWCNTs and the conducting dendrimers. These supramolecular donor-acceptor complexes, in association with poly(3-octylthiophene) were also studied with the view of using them for solar cells.<sup>26</sup>

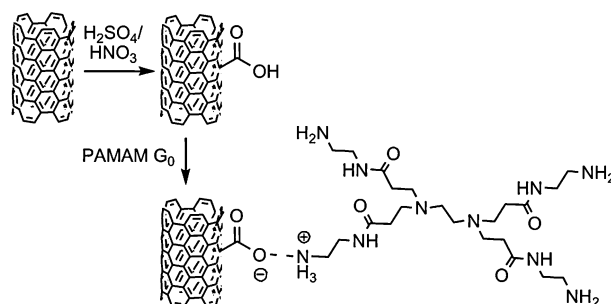


**Fig. 3** Types of dendrons and dendrimers for non-covalent interaction with single-walled carbon nanotubes.

Another type of non covalent interaction concerns ionic interactions, but in this case the SWCNTs must be first covalently functionalised. This is achieved by using nitric and sulfuric acid, which create carboxylic acid groups on the surface of SWCNTs, able for instance to interact with generation 0 PAMAM dendrimers ended by primary amine groups (Scheme 4). Adhesion of these functionalised SWCNTs in epoxy matrix is improved when compared to pristine SWCNTs, and induces a much better reinforcing effect. This association also gave satisfactory properties for the fabrication of laminated composites by vacuum-assisted resin transfer moulding (VARTM).<sup>27</sup>

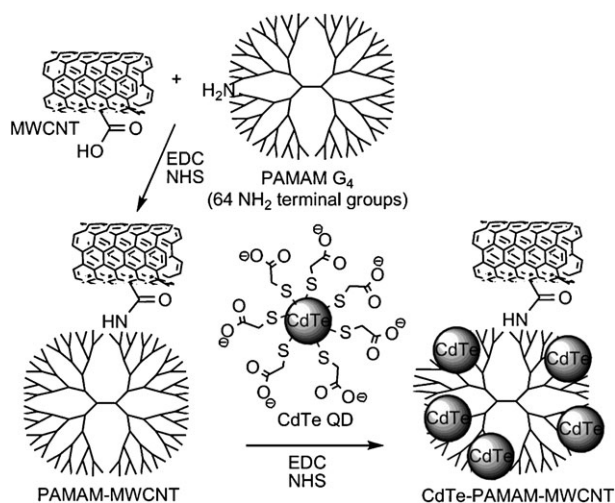
#### Connecting carbon nanotubes, dendrimers or dendrons, and nanoparticles

Several new nanocomposites were obtained by introducing a third type of nano-objects that are metal nanoparticles. Pre-synthesized CdTe quantum dots (inorganic fluorescent nanoparticles) covered by thioglycolic acid were covalently linked to PAMAM functionalised MWCNTs (Scheme 5). For comparison purposes, CdTe quantum dots (QDs) were also reacted with PAMAM dendrimers (not linked to CNTs).



**Scheme 4** Ionic interaction between a PAMAM dendrimer and an oxidized carbon nanotube.

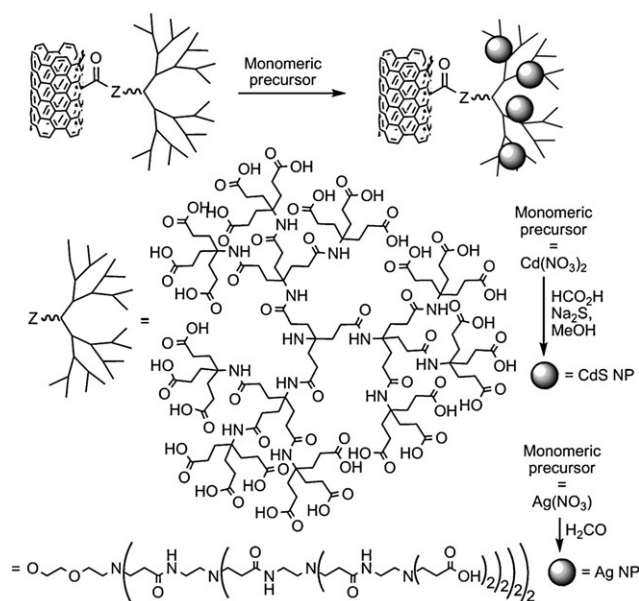




**Scheme 5** Procedure of synthesis of the nanocomposite CdTe Quantum dots-PAMAM dendrimer-Multi-walled carbon nanotubes.

It was shown that the fluorescence intensity of the CdTe-PAMAM hybrid was substantially enhanced as compared to CdTe, whereas the fluorescence was severely quenched when the QDs were attached to PAMAM-MWCNTs. The main reason for these fluorescence changes was attributed to the electron and energy transfer between the QDs and PAMAM-MWCNTs.<sup>28</sup>

However, the majority of reports connecting CNTs, dendritic structures and NPs concerns the elaboration of nanoparticles using dendrimers or dendrons linked to nanotubes. The third generation 1 → 3 C-branched amino-polyester dendron shown in Scheme 6 linked to SWCNTs was treated with Cd(NO<sub>3</sub>)<sub>2</sub> and Na<sub>2</sub>S in methanol to generate encapsulated CdS quantum dots with 1.4 nm diameter. In a blank experiment, SWCNTs were treated with Cd(NO<sub>3</sub>)<sub>2</sub> and Na<sub>2</sub>S in the same conditions, but no CdS QDs were obtained, emphasizing the



**Scheme 6** Elaboration of nanoparticles from dendrons linked to carbon nanotubes and metallic precursors.

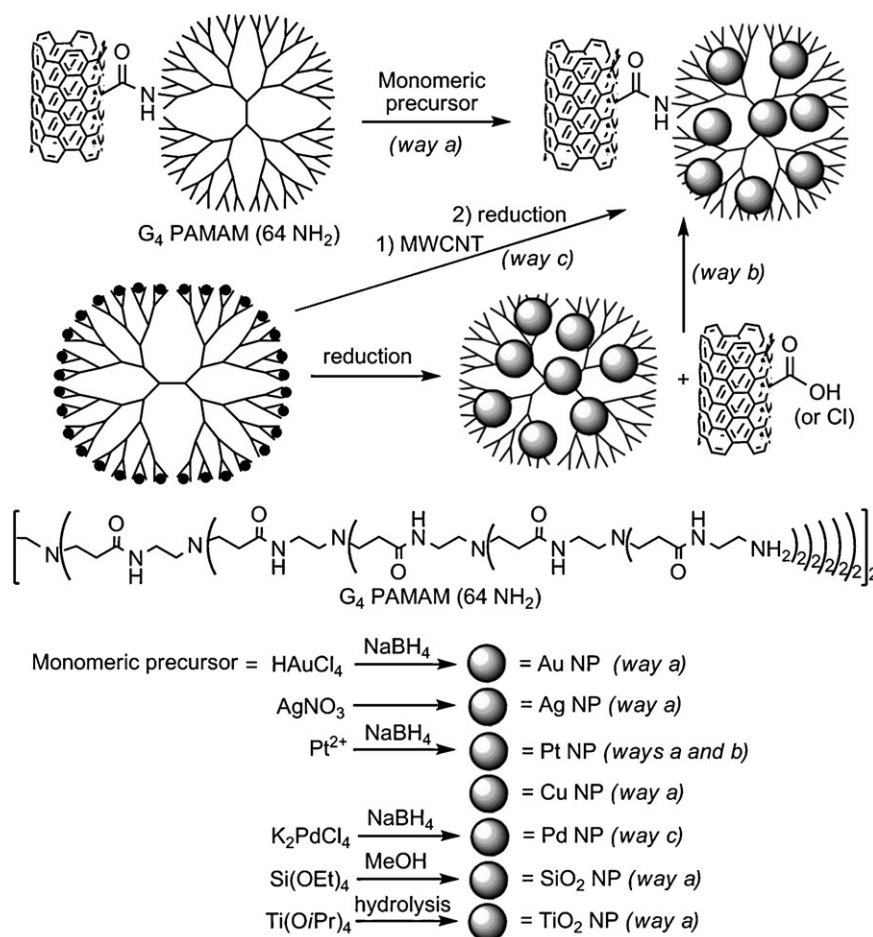
importance of the dendrons. The CdS QDs associated to the dendron-CNTs show long-term stability at 25 °C (> 90 days), but a reduced fluorescence intensity, due to partial emission quenching by SWCNTs, as indicated also above.<sup>29</sup> An analogous work was carried out with PAMAM-type dendrons linked to MWCNTs and Ag(NO<sub>3</sub>)<sub>3</sub>, leading to Ag nanoparticles (Scheme 6).<sup>30</sup>

Elaboration of dendrons is time-consuming, thus many papers deal with the use of commercially available generation 4 PAMAM dendrimers instead of dendrons. We have seen in Scheme 5 that PAMAM dendrimers can be covalently linked for functionalising CNTs; such a process was used for generating various types of nanoparticles. MWCNTs coated with G<sub>4</sub>-PAMAM are able to generate *in situ* Au nanoparticles from HAuCl<sub>4</sub>, with NaBH<sub>4</sub> as reducing agent (Scheme 7, way a). The size of the Au NPs could be tuned from 3 to 11 nm by varying the metal ion-to-dendrimer terminal amine ratio (the size increases with the amount of metal). This method was successfully generalized to produce *in situ* Cu, Ag, and Pt NPs, but also binary metal Ag/Au nanoparticles.<sup>31</sup> In an alternative method, Pt NPs were first generated from Pt<sup>2+</sup>, PAMAM-G<sub>4</sub> and NaBH<sub>4</sub>, then PAMAM-PtNPs were graft to CNTs (Scheme 7, way b). The catalytic activity of the as-prepared CNTs-PAMAM-PtNPs was tested and found highly active for oxygen reduction reactions using cyclic voltammetry (CV).<sup>32</sup> Another example of catalysis was obtained using Pd nanoparticles. In this case, K<sub>2</sub>PdCl<sub>4</sub> was first trapped by G<sub>4</sub>-PAMAM dendrimer, then the mixture was covalently anchored onto MWCNTs, and reduction with NaBH<sub>4</sub> afforded Pd NPs (Scheme 7, way c). The PdNPs-PAMAM-MWCNTs nanocomposites exhibit high electro-catalytic activity for hydrazine oxidation by CV.<sup>33</sup>

The methods used for generating metallic nanoparticles were also applied to the synthesis of SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles, from hydrolysis of the alkoxide precursors Si(OEt)<sub>4</sub> and Ti(OiPr)<sub>4</sub>, respectively. In this case also control experiments have shown that the covalently bonded dendrimers play a crucial role in the formation, fixation and growth of SiO<sub>2</sub> and TiO<sub>2</sub> NPs with sizes in the range of 35–45 nm<sup>34</sup> (Scheme 7).

### Carbon nanotubes-dendrimers for the elaboration of (bio)sensors

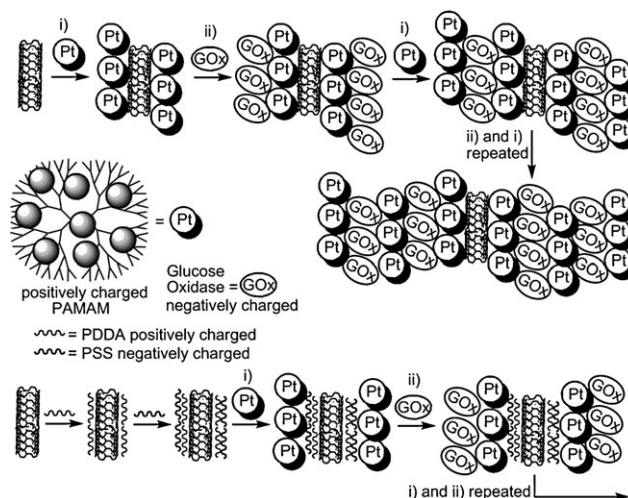
In connection with the above paragraph, Pt NPs encapsulated in PAMAM dendrimers linked to MWCNTs were found attractive materials for the elaboration of sensitive biosensors. In a first attempt, PtNPs-PAMAM-MWCNTs nanocomposites were elaborated as shown in Scheme 7 (way b), deposited onto Pt electrodes, then glucose oxidase (GOx) was attached to the broken tips of activated MWCNTs and to the terminal groups of dendrimers. Such a process afforded electrochemical sensors with remarkably improved sensitivity toward glucose.<sup>35</sup> An analogous approach was used with glutamate dehydrogenase, leading to a high sensitivity, rapid response, low detection limit (10 nM) and excellent reproducibility electrochemical sensor for the oxidation of glutamate.<sup>36</sup> However, the presence of the NPs is not mandatory; indeed PAMAM dendrimers covalently linked to CNTs and surrounded by GOx were also found useful as glucose biosensors.<sup>37</sup>



**Scheme 7** Several ways for the elaboration of nanoparticles from dendrimers linked to carbon nanotubes and monomeric precursors.

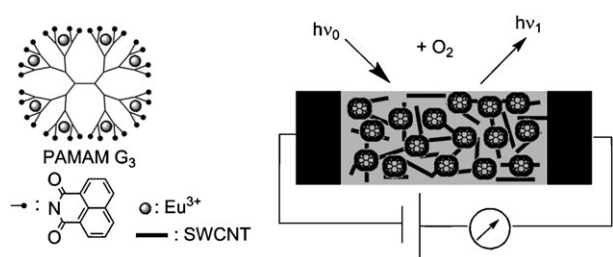
Two other approaches using the layer-by-layer (LbL) technique were applied for the elaboration of biosensors based on Pt NPs, PAMAM dendrimers and CNTs. In one case, the multi-layer was obtained by the self-assembly of Pt NPs-PAMAM and glutamate dehydrogenase (up to 8 layers were deposited) (Scheme 8, upper part). Cyclic voltammetry experiments with these multilayer nanocomposites showed that the current response increased gradually with the number of layers, but that the response time also increased.<sup>38</sup> In another multilayer approach, the PtNPs-PAMAM does not interact directly with the CNTs, but through a multilayer of poly(diallyl dimethylammonium chloride) (PDDA) and poly(sodium 4-styrenesulfonate) (PSS). Glucose oxidase was added in the last step, then up to four successive cycles of additions of Pt NPs-PAMAM and GOx were carried out, as shown in Scheme 8 (lower part). The electrocatalytic activity towards H<sub>2</sub>O<sub>2</sub> and the amperometric response of glucose on the fabricated (PtNPs-PAMAM/GOx)<sub>4</sub>/PDDA/PSS/CNTs/Pt electrodes showed that these sensors have a low detection limit, a high sensitivity, and operative stability.<sup>39</sup>

A somewhat related work was recently proposed using G<sub>3</sub>-PAMAM dendrimers functionalised with 1,8-naphthalimide as terminal groups, and entrapping not nanoparticles but 8 Eu<sup>3+</sup> cations (Eu<sub>8</sub>-PAMAM-Naph). The complex was deposited by drop-cast onto single-walled carbon nanotubes field-effect transistor devices, elaborated from quartz plates.



**Scheme 8** Two ways using the layer-by-layer technique for functionalising MW carbon nanotubes with Pt nanoparticles entrapped in PAMAM dendrimers, for elaborating amperometric biosensors.

After illuminating with 365 nm light, these devices show bimodal sensitivity (optical spectroscopy and electrical conductance) towards O<sub>2</sub> gas at room temperature and ambient pressure (Fig. 4). The proposed mechanism of this effect is that photoexcitation promotes Eu<sub>8</sub>-PAMAM-Naph ground state



**Fig. 4** PAMAM dendrimer complex of  $\text{Eu}^{3+}$  ended by naphthalimide and cartoon representation of the sensing device composed of SWCNTs and PAMAM-Eu complexes deposited on a quartz surface, for simultaneous spectroscopic and electrical conductance measurements.

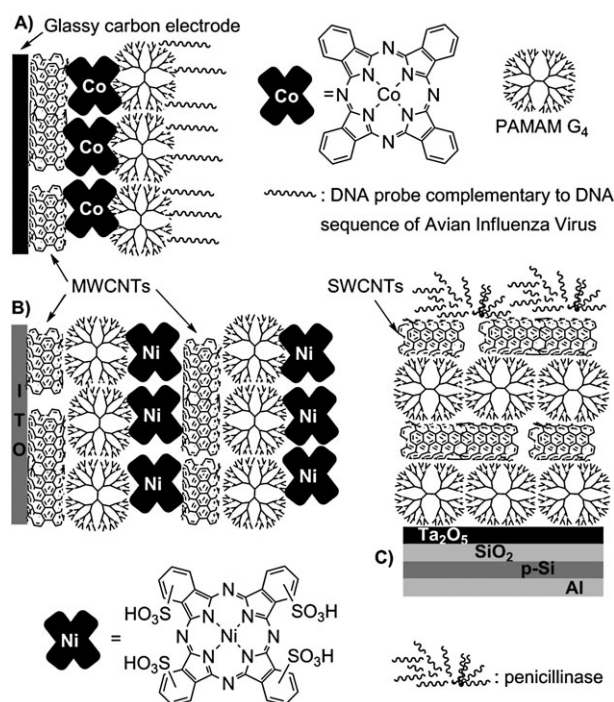
electrons in an excited state, which subsequently fill electron traps at the quartz substrate surface. The consequence is a coulombic attraction between SWCNTs valence-band electrons and the depleted  $\text{Eu}_8\text{-PAMAM-Naph}$  ground state orbital, effectively p-doping the SWCNTs valence band. Introduction of  $\text{O}_2$  induces a non-radiative relaxation pathway, allowing electrons to return from the quartz electron trap back into the  $\text{Eu}_8\text{-PAMAM-Naph}$  ground state, inducing a decrease of the emission intensity.<sup>40</sup>

Discrete metal complexes can also be covalently linked to dendrimers. The  $\text{G}_4$  PAMAM dendrimer was functionalised by ferrocene derivatives, then immobilized using poly(azetidine) pre-polymers onto MWCNTs screen printed electrode surface. Coupling to glucose oxidase induced the development of a glucose biosensor.<sup>41</sup> In other examples, CNTs, PAMAM dendrimers, and phthalocyanine (Pc) complexes were used for LbL deposition onto electrodes. In the case of the  $\text{CoPc}$  complexes, DNA probes were immobilized onto the modified electrode, with the dendrimer acting as coupling agent (Fig. 5A). A synthetic oligonucleotide related to the avian influenza virus gene was used as target complementary to the probe. The hybridization events were monitored by differential pulse voltammetry measurements based on guanine oxidation signals; the detection limit was measured at  $1.0 \text{ pg/mL}$ .<sup>42</sup>

The  $\text{NiPc}$  complexes associated with PAMAM dendrimers and MWCNTs using LbL techniques also afforded modified electrodes. The peak current for amperometric detection of the neurotransmitter dopamine was 3-fold increased in comparison to  $\text{NiPc}$  films. In addition, the detection of dopamine was possible even in the presence of ascorbic acid, which is a typical interferent (Fig. 5B). In the absence of  $\text{NiPc}$ , another LbL film was obtained, and employed in field-effect devices. These films displayed a high pH sensitivity, being capable of detecting Penicillin G ( $10^{-4} \text{ mol L}^{-1}$ ) when a layer of penicillinase was adsorbed as the top layer of the LbL film (Fig. 5C). This device is also usable as light-addressable potentiometric sensor.<sup>43</sup>

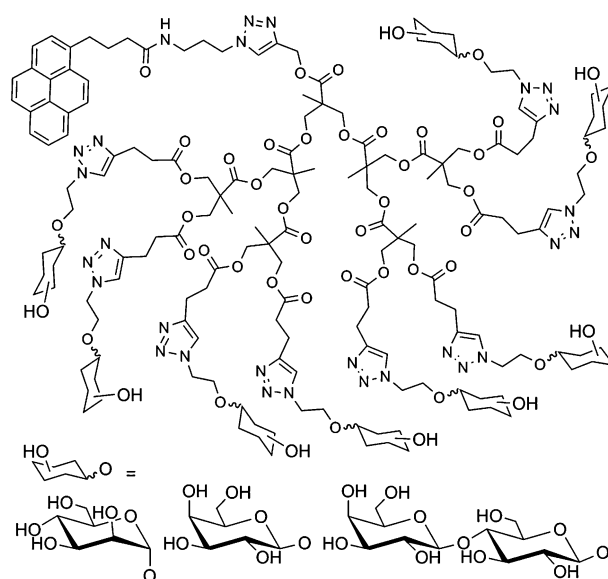
### Biological properties and uses of dendrimers-functionalised carbon nanotubes

When dealing with biological uses, the first point to be verified concerns the biocompatibility. Indeed, a number of issues associated with CNTs remain to be addressed before they can be utilized for biological applications.<sup>44</sup> Grafting



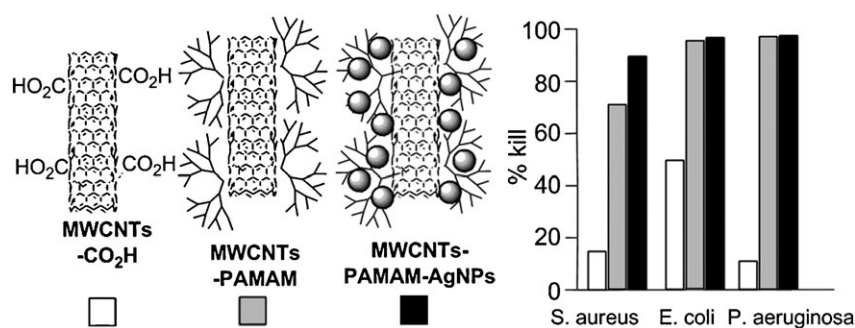
**Fig. 5** PAMAM dendrimers and CNTs used as biosensors, in connection (A, B) or not (C) with metal phthalocyanines.

biocompatible dendrons or dendrimers should induce a decreased cytotoxicity. Bifunctional glycodendrons based on 2,2-bis(hydroxymethyl)propionic acid (a biocompatible building block) having different peripheral carbohydrate units and a pyrene tail that is able to bind SWCNTs surfaces through  $\pi$ - $\pi$  interactions were elaborated (Fig. 6). HEK293 cells cultured with these glycodendrons-coated SWCNTs (up to  $100 \text{ } \mu\text{g mL}^{-1}$ ) proliferated at the same rate as cells grown in the absence of dendron-SWCNTs, contrarily to unmodified SWCNTs, which greatly hampered the growth of HEK293 cells.<sup>45</sup>



**Fig. 6** Bifunctional  $\text{G}_3$  dendrons used for non-covalent coating of SWCNTs, inducing their biocompatibility.



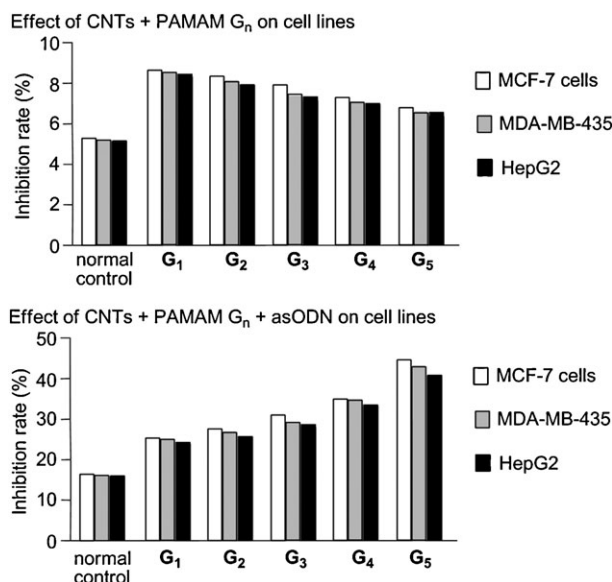


**Fig. 7** Antimicrobial activity of 3 types of functionalised carbon nanotubes: MWCNTs-CO<sub>2</sub>H (□), MWCNTs-PAMAM (■), and MWCNTs-PAMAM-AgNPs (■).

On the other hand, a certain degree of toxicity is necessary when searching for antimicrobial properties. Some PAMAM dendrimers, CNTs, and Ag NPs are known to have independently antimicrobial activities. Associating these three nano-components should induce an increase of the antimicrobial activity. MWCNTs were oxidized (functionalised by CO<sub>2</sub>H), then PAMAM dendrons (ended by NH<sub>2</sub>) were sequentially grown from these functions, and finally addition of silver acetate resulted in the formation of MWCNTs-PAMAM-AgNPs. At each of these three steps, the antimicrobial activity of these nanomaterials was tested against 3 types of microorganisms (*Staphylococcus aureus* (Gram-positive), *Escherichia coli* (Gram-negative), and *Pseudomonas aeruginosa* (Gram-negative)). The results shown in Fig. 7 demonstrate that in all cases the presence of PAMAM dendrons on the MWCNTs greatly increases the antimicrobial activity.<sup>46</sup>

The effect on murine embryonic stem cells of an analogous type of MWCNTs-PAMAM dendron (G<sub>5</sub>)-NPs, in which the NPs are fluorescent CdTe nanocrystals was tested. Observation by fluorescence microscopy, flow cytometry and MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assays indicated that these nanoassemblies could enter the cells quickly, but that they become toxic at concentrations higher than 20 μg mL<sup>-1</sup>.<sup>47</sup> However, the possibility to enter the cells makes these types of nanoassemblies attractive for transfection experiments. Indeed, the same type of association, but without NPs and with PAMAM dendrons ended by glycidyl trimethylammonium chloride was recently used for SiRNA delivery. The internalization of the nanoassemblies was demonstrated using a fluorescently labelled noncoding SiRNA sequence, the higher generation dendron (G<sub>2</sub>) being the most efficient.<sup>48</sup>

The system can be simplified using commercially available PAMAM dendrimers (as in Schemes 5 and 7), instead of step-by-step synthesized dendrons. Incubation of CNTs-PAMAM with antisense oligonucleotides (asODN) designed to be complementary to a cancer target gene induced the binding by electrostatic interactions. These nanocomposites entered adherent cell lines (MCF-7) and caused cell death and apoptosis, exhibiting an enhanced cancer cell growth inhibition (the CNTs-PAMAM alone were not found to be toxic).<sup>49</sup> CNTs-PAMAM-asODN enter into various tumour cells (human breast cancer cell line MCF-7 and MDA-MB-435, and liver cancer cell line HepG2), and inhibited the cell growth in a time- and dose dependant means, as demonstrated using FITC labelled asODN. The G<sub>5</sub> PAMAM associated with the CNTs alone was found to be the less toxic, but the most efficient gene



**Fig. 8** Growth inhibition of cancer cells by various generations of PAMAM dendrimers linked to CNTs (upper part), and by PAMAM-CNTs associated to antisense oligonucleotide (lower part).

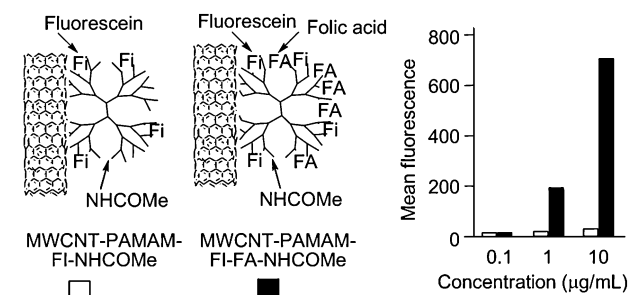
transporter and thus the most toxic when associated with the asODN, as illustrated in Fig. 8.<sup>50</sup>

Specifically functionalised PAMAM dendrimers covalently linked to MWCNTs were recently found useful for both *in vitro* cancer cells targeting and imaging. The PAMAM (G<sub>5</sub>) dendrimer was used as a multifunctional platform, since it could be functionalised with fluorescein (FI, for imaging), folic acid (FA, for targeting cancer cells overexpressing high-affinity folic acid receptors), and acetyl groups (NHAc ensuring the solubility in water and the biocompatibility). The same nanoplatform, but without folic acid, was also elaborated. The presence of folic acid induced a dose-dependent binding of MWCNTs-PAMAM-G<sub>5</sub>-FI-FA-NHAc to KB-HFAR cells (a human epithelial carcinoma cell line that over expresses high-affinity folic acid receptors) (Fig. 9).<sup>51</sup>

## Dendrimers and non-carbon nanotubes

By analogy with the functionalisation of CNTs by dendritic structures, dendrimers were used also for functionalising non-carbon nanotubes (non-CNTs). However, only a few examples





**Fig. 9** Dose-dependent binding of MWCNT-PAMAM-FI-NHCOMe (□) and MWCNT-PAMAM-FI-FA-NHCOMe (■) with KB-HFAR cells (cancerous), measured by the fluorescence intensity of fluorescein (FI).

concern this aspect, and most of the work connecting dendrimers and non-carbon nanotubes are about the elaboration/synthesis of non-CNTs with or by dendrimers. Contrarily to what we have seen with CNTs, PAMAM dendrimers and dendrons were rarely used in connection with non-CNTs; instead, a rich diversity of dendritic structures was used.

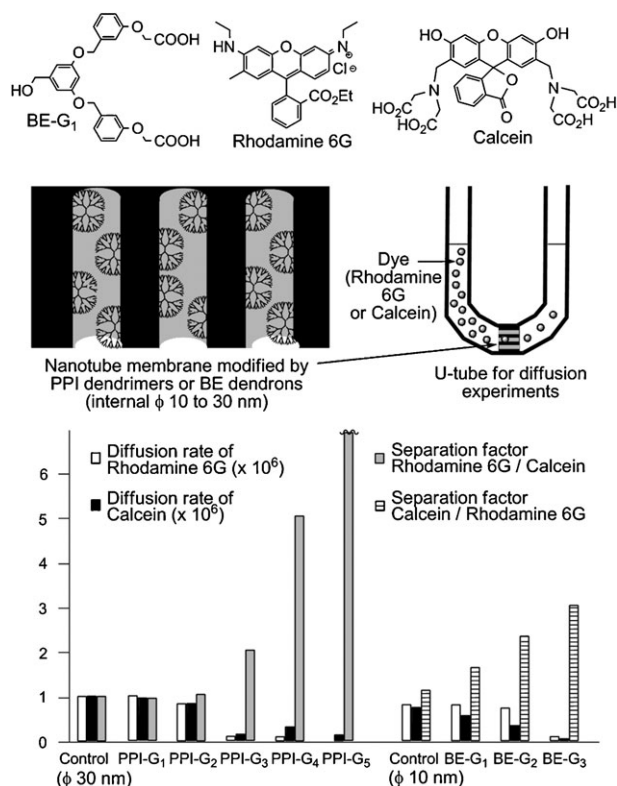
#### Interactions of dendrimers with pre-existing non-carbon nanotubes

Very recently, boron nitride nanotubes (BNNTs) obtained by a CVD process were coated with glycodendrons of type shown in Fig. 6 ( $G_2$  ended by  $\alpha$ -mannose moieties). The specific binding of BNNTs- $G_2$ Man was assessed towards  $\alpha$ -mannose-specific receptor *Canavalia ensiformis* agglutinin conjugated to FITC (fluorescein), and towards a lectin that does not recognize mannose (*Helix pomatia* agglutinin conjugated to FITC). Clear ligand-receptor interactions were observed in the first case, while resistance to nonspecific binding of irrelevant protein was observed in the second case.<sup>52</sup>

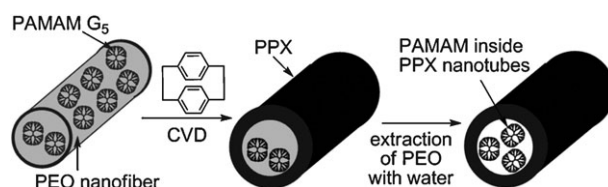
Membranes composed of polymer nanotubes were functionalised inside the nanotubes by dendrimers or dendrons. The interior of poly(vinylpyrrolidone) (PVP) nanotubes was first reacted with  $Sn^{2+}$ , then by a layer of poly(acrylic acid), then by a layer of positively charged PPI (poly(propyl-imine)) dendrimers. Starting from a 30 nm diameter of the pores of PVP, these layers reduced the diameter to 26 nm with PPI- $G_1$  to 13 nm with PPI- $G_4$  (Fig. 10).

These modified membranes were used for recognition of two dyes (positively charged rhodamine 6G, and negatively charged calcein). Upon functionalisation with PPI- $G_1$  and PPI- $G_2$ , there was no discernible difference between the rates of diffusion of the two dye molecules when compared to unfunctionalised membrane (control). However, significant differences were observed when using PPI- $G_3$ , PPI- $G_4$  and PPI- $G_5$ , with calcein being favoured. An analogous work was carried out with anionic benzylether dendrons (BE- $G_1$  to BE- $G_3$ ) instead of cationic PPI dendrimers. In these cases, the diffusion of rhodamine 6G was favoured (Fig. 10).<sup>53</sup>

Very recently, poly(ethylene oxide) (PEO) nanofibres were covered by PAMAM  $G_5$  dendrimers then CVD of [2,2]-paracyclophane induced the coating of the PEO-PAMAM fibres by poly(paraxylene) (PPX). Extraction of PEO with water afforded nanotubes of PPX containing the PAMAM dendrimers



**Fig. 10** Interior of poly(vinylpyrrolidone) nanotubes-membrane functionalised by PPI dendrimers (see Scheme 2 for their structure) or benzylether dendrons (BE), and their use for selective recognition of two dyes.



**Scheme 9** Elaboration of poly(paraxylene) (PPX) nanotubes containing PAMAM dendrimers inside.

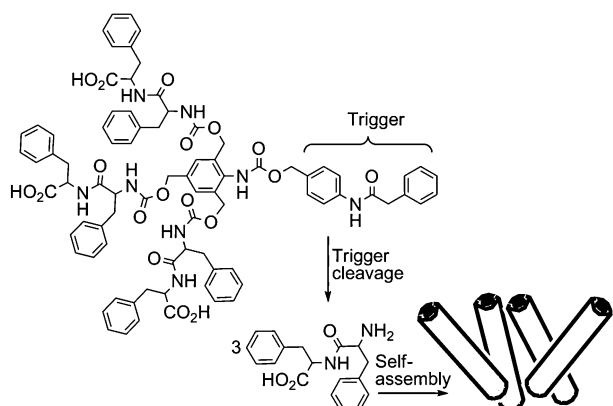
(Scheme 9). No leaching of PAMAM  $G_5$  was observed after immersing the nanotubes in water (or DMSO) for 3 days, whereas the leaching of PAMAM  $G_4$  occurred in a few hours. PPX-PAMAM  $G_5$  non-CNTs were used for two types of catalytic reactions. In a first attempt the Knoevenagel condensation of malonodinitrile with benzaldehyde was performed at 0 °C, with 10 mol% of  $NH_2$  (from PAMAM) as catalyst; 81% yield was obtained after the first as well as the tenth run, emphasizing the stability and the reusability of this original catalytic system. In another experiment, TEMPO moieties were grafted to some terminal  $NH_2$  groups of PAMAM  $G_5$  (ca. 26% of the terminal amines were functionalised). These modified PAMAM dendrimers inside the nanotubes were used to catalyze the oxidation of benzyl alcohol to benzaldehyde (2.1 mol% of nitroxide) in quantitative yield. This catalyst was remarkably reused 17 times without loss of activity.<sup>54</sup>

### Synthesis of non-carbon nanotubes from (self-)assembly of dendrimers or dendrons

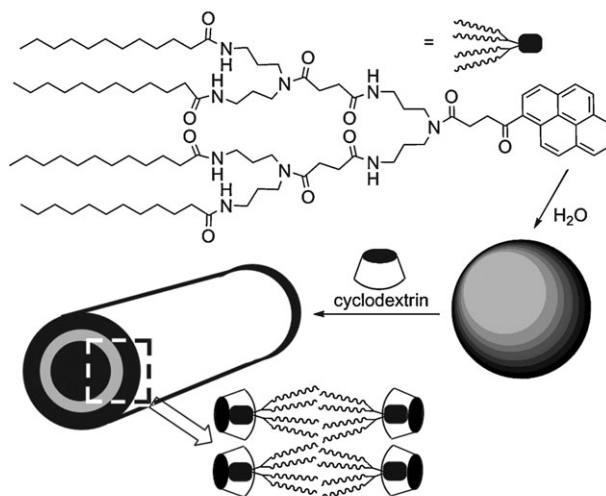
Diversified examples of nanotubes built using dendrimers are known. In some cases, the dendrimer is an adjuvant, not included in the structure of the nanotube. For instance, the template-free synthesis of poly(aniline) tubules was obtained by polymerisation of aniline in the presence of PAMAM-G<sub>4</sub> dendrimers functionalised by naphthyl-SO<sub>3</sub>H terminal groups, acting as protonic acid dopant.<sup>55</sup> The dendritic structure also can be destroyed to elaborate the nanotubes. Indeed, peptide nanotubes were obtained by enzymatic activation of self-immolative dendrons, having diphenylalanine end-units and a trigger designed for activation by PGA (penicillin G amidase) as core. A cascade enzymatic cleavage resulted in well-ordered nanotubes of diphenylalanine; no organized structure was observed when the peptides are attached to the dendron (Scheme 10).<sup>56</sup>

There also exist examples in which the nanotubes are created by the (self-)assembly of dendrimers having a particular core. An amphiphilic rigid macrocycle used as core of a small oligo(ethylene glycol) dendrimer (Fig. 11) was shown to self-assemble into tubular aggregates, thanks to  $\pi$ - $\pi$  stacking interactions between aromatic units. These supramolecular tubules were shown to solubilise SWCNTs in water, whereas the non-aggregated macrocycles did not.<sup>57</sup>

Organic nanotubes were obtained by a two-step supramolecular self-assembly, starting from an amphiphilic dendron



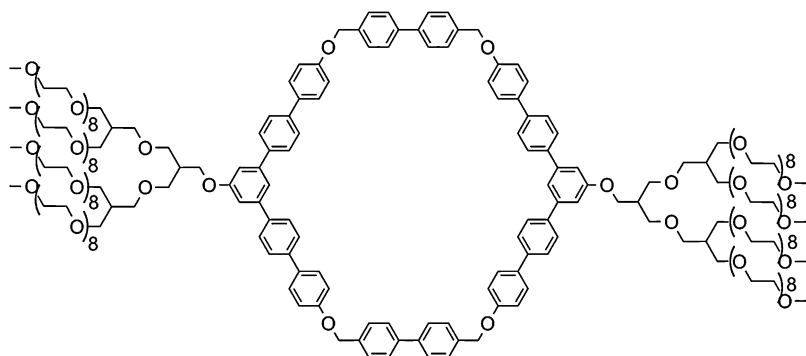
**Scheme 10** Self-assembly of diphenylalanine peptide nanotubes after enzymatic cleavage of a self-immolative dendron.



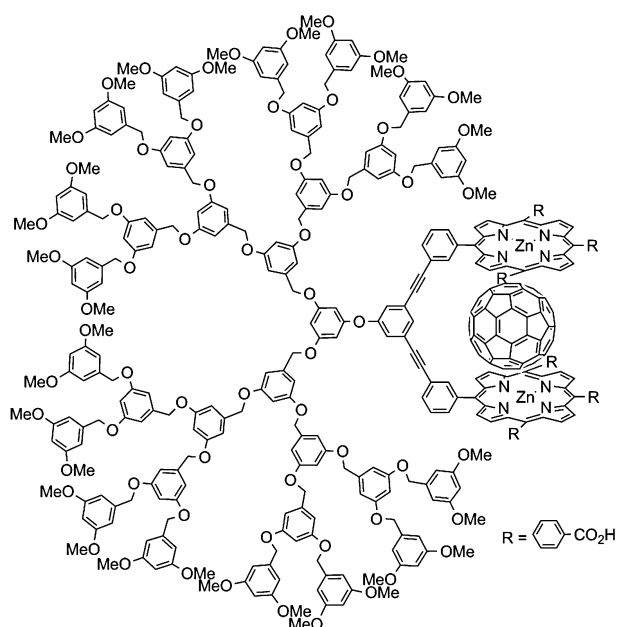
**Scheme 11** Schematic route to organic nanotubes. Amphiphilic dendron-pyrenes form vesicles in water. Addition of cyclodextrin transforms the vesicular organization to nanotubes.

possessing a pyrene as core. Addition of water creates vesicular organizations stable for several months in aqueous phases, with water entrapped in the interior of the vesicles. Fluorescence spectra suggest that the focal pyrene units are pre-organized to form excimers. Addition of cyclodextrin (CD) induces the supramolecular transformation of vesicles into nanotubes. This is due to the introduction of the focal pyrene units into the CD, which makes the focal moiety very hydrophilic, interrupts the formation of pyrene excimers, and induces the supramolecular rearrangement shown in Scheme 11. The bilayer structure undergoes helical transformation, and then forms tubular architectures. The surface functionalities of the nanotubes could be modified using functionalised cyclodextrines to obtain for instance nanotubes-nanoparticles supramolecular assemblies, and biomolecular sensors for the detection of proteins when attaching biotine to the nanotubes.<sup>58</sup>

Metallated dendritic porphyrins are also suitable for obtaining nanotubes due to their tendency to aggregate. However, this tendency has to be favored by polymerization reactions. Two porphyrins linked to the core of a poly(arylether) dendrimer functionalised with 3 carboxylic acids were used to trap fullerene. Two of the three carboxylic acids interact with fullerene, the remaining is usable for dimerizations to induce



**Fig. 11** Amphiphilic macrocycle able to self-assemble through  $\pi$ - $\pi$  stacking interactions.



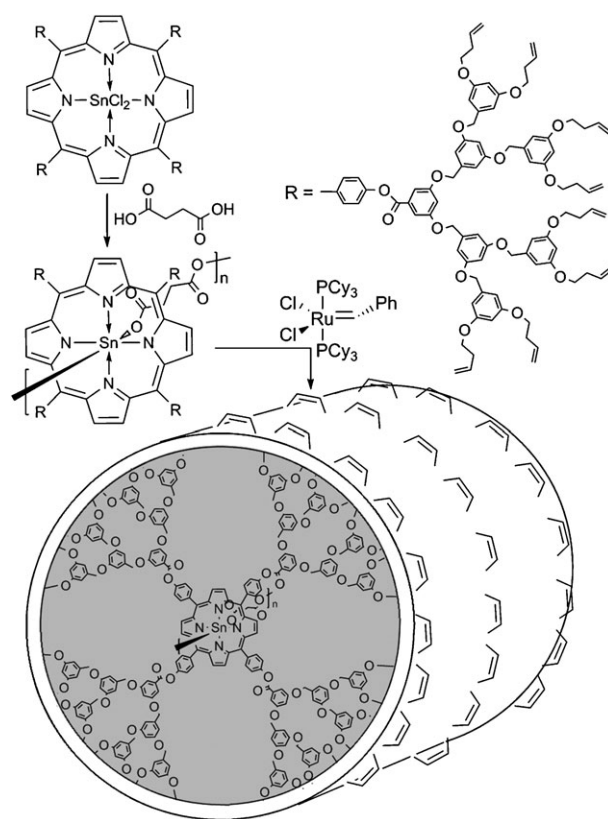
**Fig. 12** Structure of the porphyrin dendrimer encapsulating fullerene. One R ( $\text{C}_6\text{H}_4\text{CO}_2\text{H}$ ) on each porphyrin is then used for dimerization reactions, inducing the linear polymerization of the dendrimers.

the unidirectional polymerization of the complex (Fig. 12), producing nanotubes (or more probably fibres) with 15 nm diameter.<sup>59</sup>

The polymerization can be induced also through the metal inside the porphyrin; in particular  $\text{SnCl}_2$  can react with succinic acid, which becomes the bridging bidentate ligand, to obtain oligomers (essentially tetramer to dodecamer). The alkene terminal groups of the oligomers were used for inter-dendrimer cross-linking by ring closure metatheses catalyzed by a Grubbs ruthenium catalyst. In the final step, the internal oligoporphyrin core was removed through a transesterification reaction with NaOMe to afford real nanotubes (with an “empty” interior) (Scheme 12).<sup>60</sup>

### Synthesis of non-carbon nanotubes by layer-by-layer assembly of dendrimers

As we have seen previously, the LbL method necessitates oppositely charged entities. Non-carbon nanotubes constituted exclusively of dendrimers were obtained using two types of generation 4 phosphorus dendrimers, ended either by ammonium groups or by carboxylate groups. Nanotubes were obtained by a direct layer-by-layer deposition of these charged dendrimers within the pores of ordered porous alumina (anodic aluminium oxide). The walls were first coated with 3-aminopropyl dimethylethoxysilane (3-APDMES), which provides a positively charged surface. A monolayer of negatively charged dendrimers was directly deposited by immersing the template into the solution of dendrimer, then rinsing with water. The same process was repeated with positively charged dendrimers, and so on, up to 20 bilayers. The non-carbon nanotubes were released by applying a solution of chromium(III) oxide in phosphoric acid

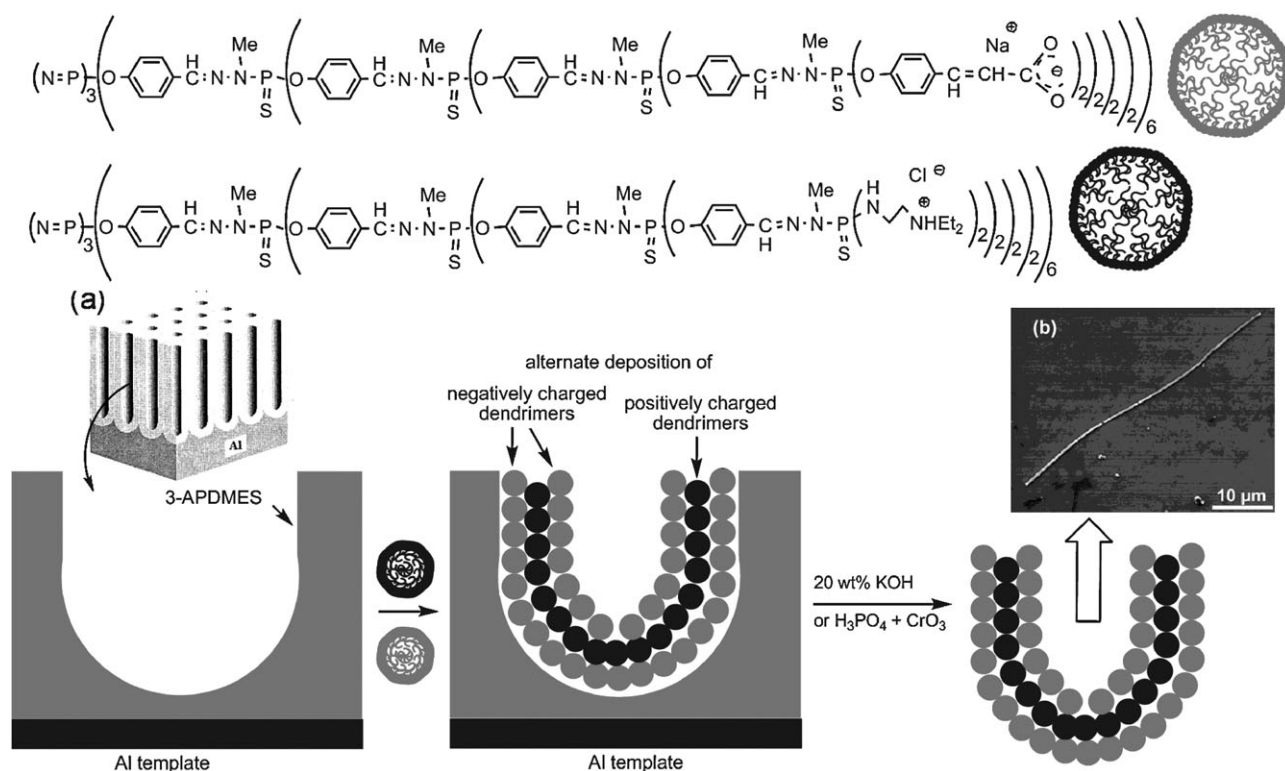


**Scheme 12** Assembly of porphyrin dendrimers, then polymerization of the terminal alkene groups to rigidify the nanotube. The porphyrins can be removed by reaction with NaOMe to afford a real nanotube.

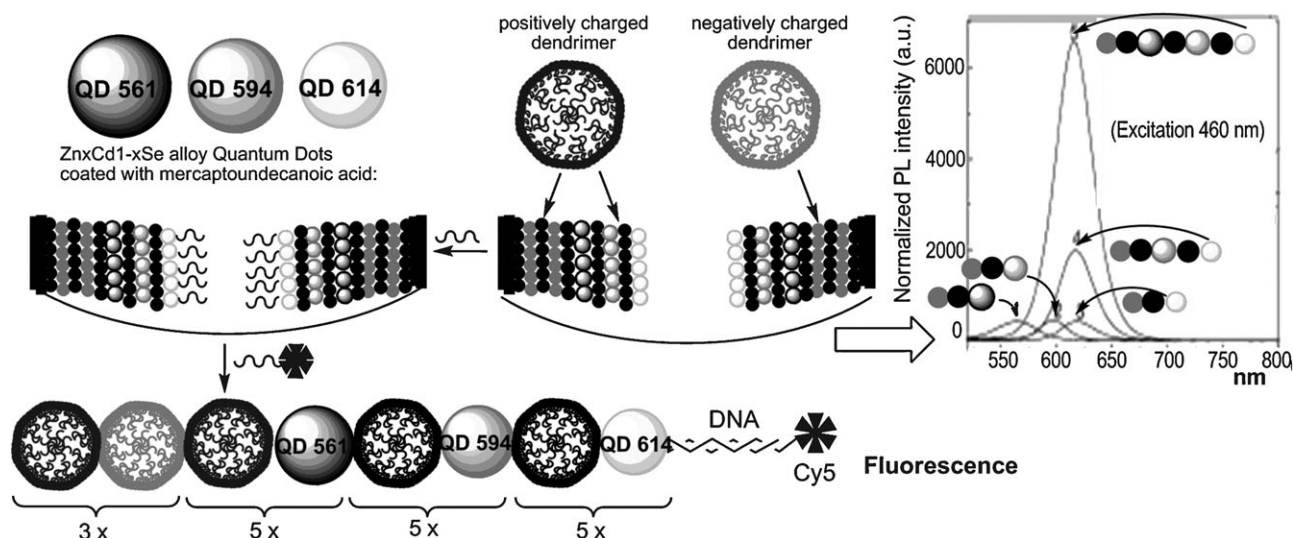
or 20% potassium hydroxide. The template is destroyed and the nanotubes made of dendrimers are the replica of the template pores (diameter 400 nm, length 80  $\mu\text{m}$ , with a wall thickness of 40 nm) (Fig. 13).<sup>61</sup>

Using the same principle, negatively charged quantum dots constituted of ZnCdSe alloys in various proportions, and emitting at 561, 594, or 614 nm were used at some layers instead of negatively charged dendrimers. When a single type of QD was used, the non-CNTs emitted at the wavelength of the QD. When 2 or 3 different quantum dots were used at some layers of the non-CNTs, by controlling the distance between the layers of QDs, funnel-like bandgap profiles can be realized, which display rapid and efficient fluorescence energy transfer (FRET) along the bandgap gradient. Indeed, when using  $\text{QD}^{561}$ ,  $\text{QD}^{594}$ , and  $\text{QD}^{614}$ , only the emission of  $\text{QD}^{614}$  could be detected. Such property was used for sensitive detection of DNA hybridization. For this purpose, an additional internal layer was obtained by coupling amino end-group-derivatized probe DNA strands (30, 50, or 80 bases) to N-hydroxysuccinimide-activated carboxylic groups of  $\text{QD}^{614}$  layer forming the inner surface of the walls of the nanotubes. A fully complementary 15-mer DNA oligonucleotide sequence labelled with the dye Cy-5 could be hybridized. Surface plasmon resonance spectroscopy and photoluminescence spectroscopy gave clear evidence of the hybridization, with an excellent detection limit of 10 fM ( $10^{-14}$  M) (Fig. 14).<sup>62</sup>





**Fig. 13** Chemical structure of phosphorus dendrimers ended by carboxylate or ammonium groups. Elaboration of dendrimers nanotubes from nanoporous alumina template (a) positively charged by APDMES the alternate and successive deposition of phosphorus dendrimers ended by carboxylates or ammonium. Removal of the template by KOH or  $H_3PO_4 + CrO_3$  affords the dendrimers nanotubes as seen in (b).



**Fig. 14** Funnel-like bandgap profiles obtained from the association of ZnCdSe quantum dots and dendrimers. The right part displays the photoluminescence spectra of several associations.

## Conclusions

The melding of dendrimers and nanotubes is an emerging research interface, which covers very different aspects of chemistry and nanosciences. In most cases, this association has utilized carbon nanotubes and PAMAMs but there are many other systems that are being created. Diverse uses such as the elaboration of CNTs from nanoparticles elaborated

thanks to the dendrimers, the functionalisation of the CNTs by the dendrimers to increase their solubility, their combination for the elaboration of field effect transistors and sensitive biosensors, and the functionalisation with dendrimers to lower the toxicity of CNTs or enhance their antimicrobial activity have been successfully explored up to now.

A still newer area of research concerns dendrimers and non-carbon nanotubes. Examples about the elaboration of specific

filters and of highly efficient catalysts obtained from existing non-CNTs functionalised by dendrimers were reported. However, most examples concern the elaboration of non-CNTs constituted by the self-assembly of dendrimers, either spontaneously or using the layer-by-layer technique. This field is still in its infancy and very few uses of such devices were reported, with the notable exception of the non-CNTs constituted of phosphorus dendrimers and quantum dots, which display an excellent detection limit (10 fM) for DNA hybridization.

In view of these promising results, there should be plenty of room for high level research connecting dendrimers and CNTs or non-CNTs, which should be of interest for chemists, physicists, and biologists.

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