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Functionalization of CNT: Synthesis and applications in photovoltaics and biology

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ABSTRACT: Here, we review part of the work carried out in our laboratories on carbon nanotube functionalization. Both covalent (sidewall derivatization) and non-covalent (using π-π interactions) functionalization have been used to solubilize carbon nanotubes (NTs). The combination of NTs with various electron donors, mainly using the supramolecular approach, led to a new generation of donor-acceptor nanohybrids which can be used for the development of carbon-based photovoltaic cells. Covalent functionalization has been successfully applied for preparation of water soluble nanotubes and further derivatization of the nanotubes with bioactive molecules hold great promise for application in drug, vaccine and gene delivery. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: Carbon nanotubes; functionalization; electron transfer; photovoltaic; drug delivery; vectors; peptides; cells; toxicity

INTRODUCTION

Carbon nanotubes (NTs) are cylindrically shaped nanostructures that have radii as small as tenths of nanometers. Historically, multi-walled nanotubes (MWNTs) were first discovered in 1991,[1] followed later in 1993 by their single-walled analogous.[2,3] Single-walled nanotubes (SWNTs) possess the simplest geometry (i.e., a rolled-up graphene sheet that is closed by semi-fullerene-like caps) and their diameters typical range between 0.8 and 2 nm. MWNTs, on the other hand, are composed of a concentric arrangement of numerous cylinders reaching diameters of up to 100 nm.

Ideally, SWNTs possess distinct regions of different chemical reactivity. Obviously, the implementation of five-membered rings into the region of caps brings about a high reactivity towards chemical functionalization. Chemical functionalization of the sidewall—comprising regularly structured/shaped graphene framework—renders a lot more difficult. In general, addition reactions to carbon–carbon double bonds cause a transformation of sp^2-hybridized carbon atoms into sp^3-hybridized analogous. Such dramatic changes are associated with the modification of the predominantly trigonal-planar local bonding geometry into a tetrahedral geometry. Importantly, this process is energetically more favorable in the cap region due to the pronounced two-dimensional curvature, while the sidewalls reveal a comparatively low one-dimensional curvature.

Carbon nanotubes are usually generated by (i) arc discharge, (ii) laser ablation or (iii) catalytic gas-phase growth starting with carbon monoxide or other carbon sources. The raw material contains carbon nanotubes contaminated with different amounts of amorphous carbon and/or catalytic metal particles. Consequently, the necessity evolves to perform an effective purification process prior to their use/further processing. Treatment of the crude materials, for example, under strong acidic and oxidative conditions constitutes a powerful approach. In particular, sonication in a mixture of concentrated nitric and sulfuric acid or heating in a mixture of sulfuric acid and oxygenated water give rise to the formation of small dimension opened tubes.[4,5] Result of these oxidation methods is the introduction of carboxyl groups, which is, however, not limited to the caps but also occurs at the defect sites along the sidewalls. Additionally, such an approach opens the way for further modifications of SWNTs or MWNTs, since acid functionalities react with alcohols or amines to give rise to ester or amide linkages, respectively. Notably, this functionalization method leads to a partial loss of electronic structure/optical properties of the NTs and a loss of material due to the oxidative process.

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In our groups we focus on the functionalization of carbon nanotubes towards biological[6,7] and electronic/photovoltaic applications.[8] For this reason, we have established two complementary strategies—either covalent sidewall functionalization[9–12] or non-covalent sidewall functionalization[13,14]—which are based on a molecular or a polymer approach. Eventually, the two approaches may lead to similar results, but they differ in the degree of involvement of the carbon skeleton in the formation of covalent bonds. Covalent functionalization results in a change of hybridization from sp^2 to sp^3 and in a possible partial loss of conjugation with effects on the electron-acceptor and/or electron-transport properties.

CARBON NANOTUBES FOR ELECTRON TRANSFER AND PHOTOVOLTAIC APPLICATIONS

Pure supramolecular approach

Amphiphilic pyrene derivatives are known to disperse carbon nanotubes through π-π interactions.[13] Using 1-(trimethylammonium acetyl)pyrene bromide (pyrene$^+$), we were able to disperse SWNTs and MWNTs in aqueous media (Scheme 1).[15,16]

The TEM analyses of SWNT/pyrene$^+$ and MWNT/pyrene$^+$ show in the first case bundles of NTs with diameters of 25 nm and lengths of several micrometers and for MWNT/pyrene$^+$ individual nanohybrids with diameters ranging between 20 and 30 nm and lengths of several micrometers. In Fig. 1a and b we compare the UV, Vis, and NIR absorption spectra of pyrene$^+$ and SWNT/pyrene$^+$. The absorption spectra of an aqueous SWNT/pyrene$^+$ solution reveal several important features. First, the π–π transitions of pyrene$^+$ are slightly red-shifted (i.e., 1–2 nm) which indicates that electronic communication between the two different ring systems occurs. Second, the overall absorption cross-section increases, particularly in the Vis- and NIR-regions. Third, the characteristic van Hove singularities of SWNTs are discernable in the Vis-NIR region up to around 450 nm, where the π–π* transitions of pyrene$^+$ dominate the spectrum (Fig. 1).

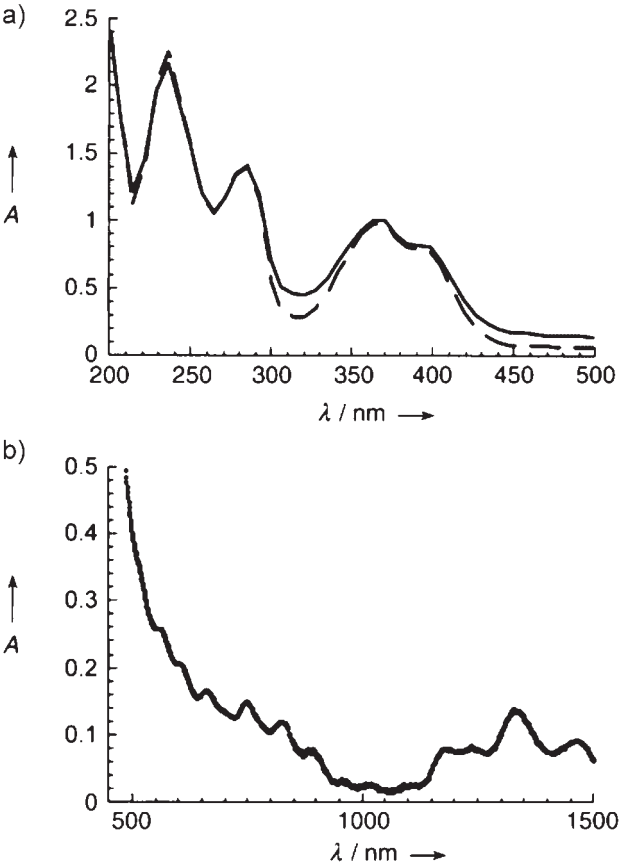
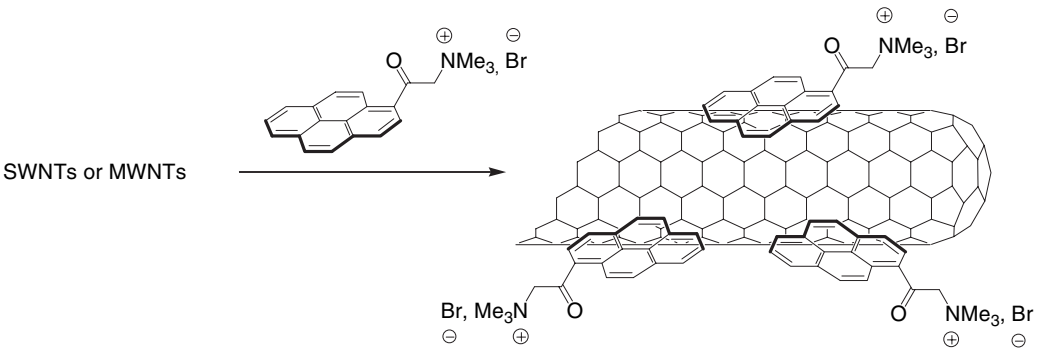


Figure 1. (a) absorption spectra of pyrene$^+$ (dashed line) and SWNT/ pyrene$^+$ (solid line) in H_2O; (b) absorption spectra in the Vis-NIR region of SWNT/ pyrene$^+$ in D_2O

To prepare donor–acceptor complexes the trimethylammonium group of pyrene$^+$ was used as an electrostatic anchor to bind anionic porphyrin derivatives (H_2P^{8-} and ZnP^{8-}) (Fig. 2). For the supramolecular association between the porphyrin (i.e., H_2P^{8-} or ZnP^{8-}) and the NT with pyrene (i.e., SWNT/pyrene$^+$ and MWNT/pyrene$^+$), which was followed spectroscopically, binding constants were derived that were on the order of $10^4\,M^{-1}$.[8] For ZnP^{8-}, the fluorescence quantum yield is 0.04 and the lifetime is 2.1 ± 0.2 ns, and for H_2P^{8-}, the fluorescence quantum yield is 0.11 and the lifetime is 9.4 ± 0.5 ns.[15] In the composite systems, fluorescence and transient absorption studies in solutions showed rapid intrahybrid



Scheme 1. Schematic representation of carbon nanotubes with positively charged pyrene

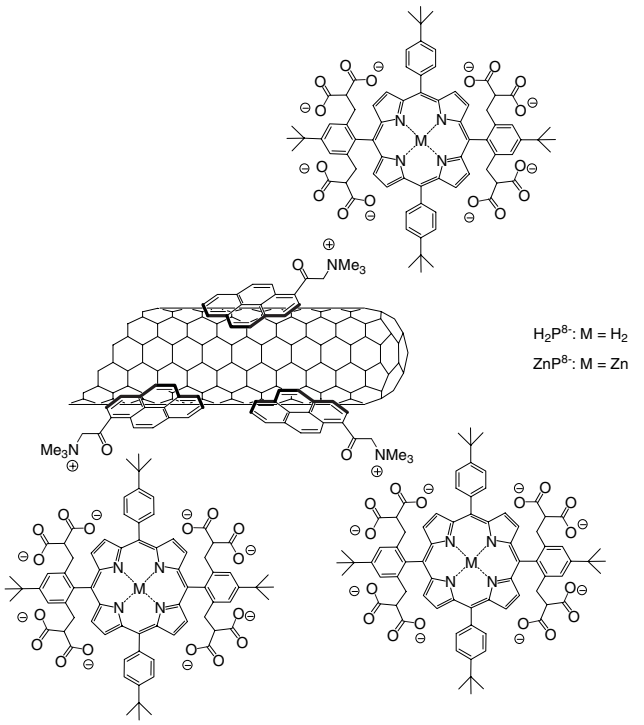


Figure 2. SWNT with positively charged pyrene and negatively charged porphyrins

electron transfer (0.2 ± 0.05 ns), creating intrinsically long-lived radical ion pairs. Following the initial charge separation event the spectroscopic features of the oxidized donors disappear with time. Through the analysis of several wavelengths, it was possible to obtain a lifetime for the newly formed ion-pair state of 0.4 ± 0.05 μs.

The large number of concentric graphite sheets in MWNT renders them more efficient electron acceptors/electron carriers compared to SWNT. In addition, MWNTs are easier to process because they do not form big bundles usually observed with SWNT and, therefore, facilitating the dispersion of MWNT with pyrene^{+} in water. We pursued the supramolecular assembly of MWNT/pyrene^{+}/ZnP^{8-} in a similar way to what we established for SWNT. Photoexcitation of MWNT/pyrene^{+}/ZnP^{8-} also gave rise to charge separation and lifetimes for the radical ion pair state of the order of microseconds (5.8 ± 0.2 μs).[16] The better delocalization of electrons in MWNT, relative to SWNT, is most likely the reason for longer lifetimes. Percolation of the charge inside the concentric wires decelerates the decay dynamics of the charge recombination.

We also demonstrated that it was possible to invert the charges of the pyrene and of the porphyrin. For this work we used a negatively charged pyrene (pyrene^{-}) and positively charged porphyrins (Fig. 3).[17] The interactions between SWNT and pyrene^{-} were investigated by absorption spectroscopy. The maxima of the pyrene^{-} transitions in the 200-400 nm region are shifted by about 2 nm, which suggests mutually interacting π-systems.

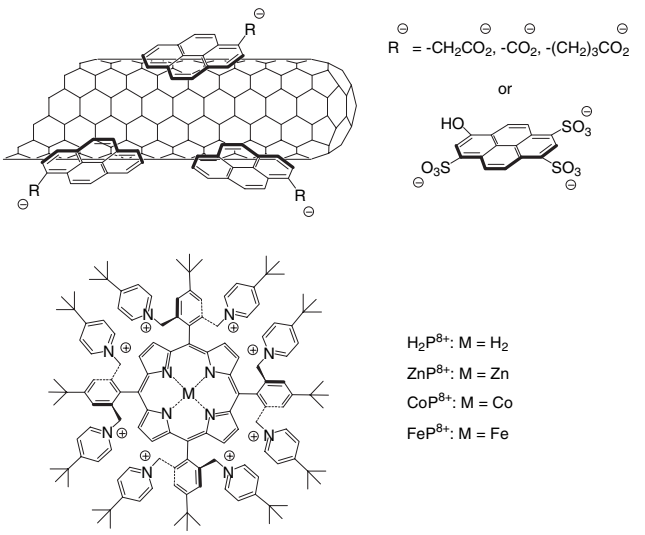


Figure 3. SWNT with negatively charged pyrene and positively charged porphyrins

Electrostatic interactions between negatively charged SWNT/pyrene^{-} and positively charged porphyrins MP^{8+} (i.e., M = H_2, Zn, Fe, and Co) were tested in a series of investigations. These include microscopy (i.e., TEM and AFM) and spectroscopy (i.e., absorption and fluorescence spectroscopy). The time-resolved fluorescence and transient adsorption measurements of the SWNT/pyrene^{-}/MP^{8+} confirmed that upon photoexcitation a rapid intrahybrid charge separation takes place. The radical ion pairs are long-lived, with microsecond lifetimes.

Hybrid covalent/supramolecular approach

In this approach, SWNTs were first functionalized with sodium poly(styrene-4-sulfonate)[18] (PSS) to form SWNT-

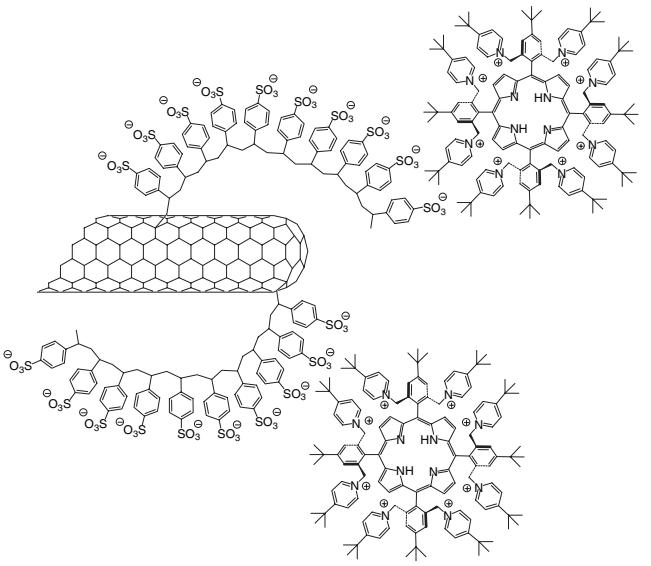


Figure 4. SWNT functionalized with PSS^{n-} and positively charged porphyrins

PSS^{n-} and the negative charges on the polymer were used to form an electrostatic complex with H_2P^{8+} (Fig. 4).

The polymer covalently linked on the sidewall ensures the solubility of the NTs in water. The ratio of NTs and polymer was estimated of 55:45, but since only a limited number of polymer chain are attached on the NTs, the absorption spectra showed that the electronic fine structure of the SWNTs is maintained in the Vis-NIR region. The complexation of SWNT-PSS^{n-} with H_2P^{8+} was followed by absorption and fluorescence spectroscopy. In the complex, photoexcitation of the porphyrin chromophore is followed by a rapid and efficient intrahybrid charge separation event, for which we detected a radical ion-pair state. Under unaerobic conditions, a lifetime of 14 μs was observed for the newly formed ion pair.[19] This is the longest lifetime reported for the systems discussed in this review.

Design of devices

The favorable charge separation features that result from the combination of SWNT with porphyrins in SWNT/$pyrene^{+}$/ZnP^{8-} and SWNT-PSS^{n-}/H_2P^{8+} are promising for the construction of photoactive electrode surfaces. Using electrostatically driven layer-by-layer (LBL) assembly technique, we realized semitransparent ITO electrodes from SWNT/$pyrene^{+}$/ZnP^{8-} and SWNT-PSS^{n-}/ZnP^{8+}. The ITO electrodes were first coated by poly(diallyl dimethylammonium) chloride ($PDDA^{n+}$) or sodium poly(styrene-4-sulfonate) (PSS^{n-}); the hydrophobic interactions between the surface and the polymer chains ensure the stability of the modified electrode on which the NTs will be deposited. After deposition of a layer of SWNT/$pyrene^{+}$ or SWNT-PSS^{n-} on PSS^{n-} or $PDDA^{n+}$ coated ITO, respectively, the layer of negatively or positively charged porphyrin is deposited. The different steps of the construction of the electrode were investigated by optical spectroscopy on quartz slides and by AFM on silicon wafers (Fig. 5).

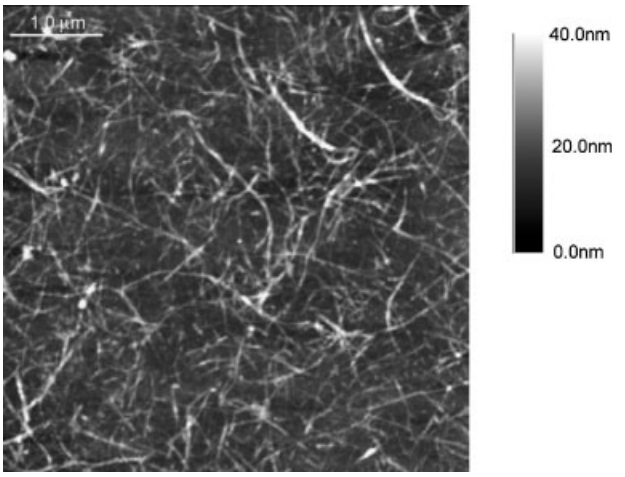


Figure 5. AFM picture of SWNTs (on silicon wafer) during the deposition process; image size 5 μm × 5 μm

The cell is finally constituted by a Pt electrode connected to the modified ITO electrode in a solution of sodium ascorbate. Upon illumination, electron transfers from the porphyrins to the NTs occur; the electrons are then injected in the ITO and travel to the Pt electrode. The oxidized porphyrins are converted to their ground state through the reduction via sodium ascorbate, which serves as a sacrificial electron donor (Fig. 6). These systems give

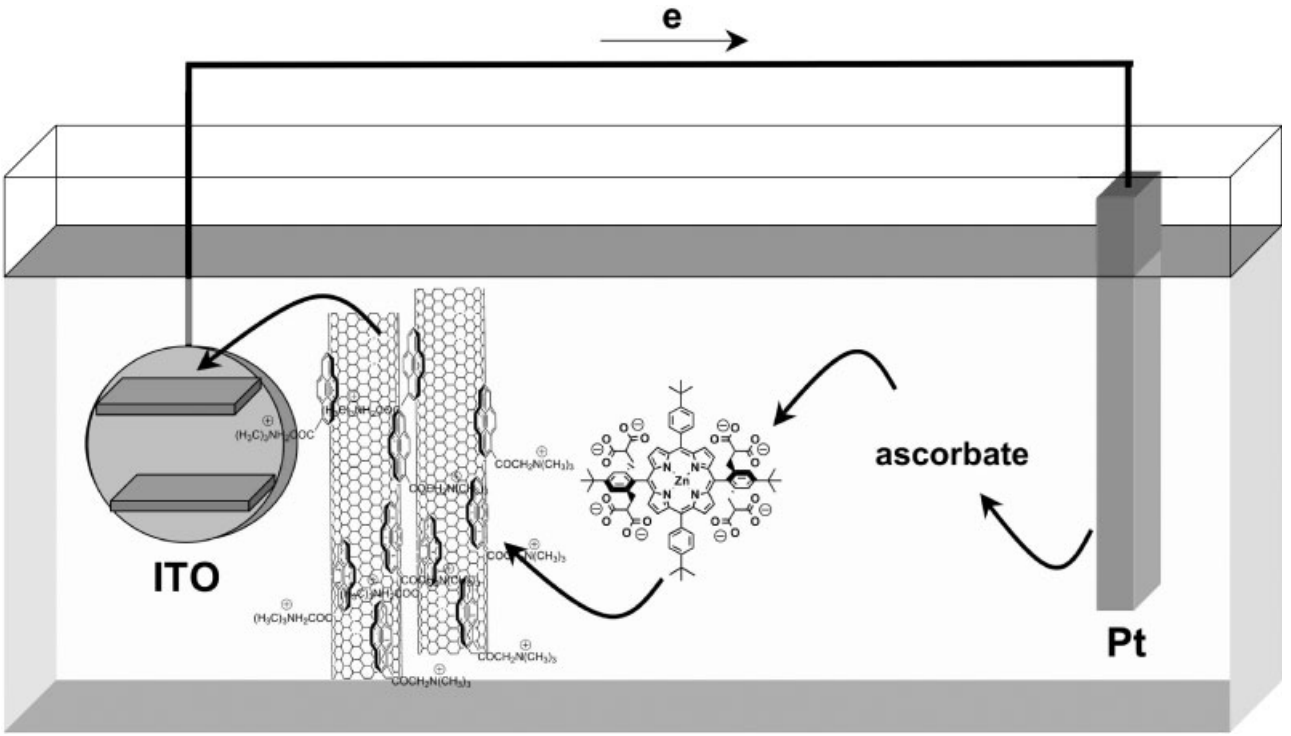


Figure 6. Schematic illustration of photocurrent generation in ITO electrodes covered with a single SWNT/$pyrene^{+}$/ZnP^{8-} stack

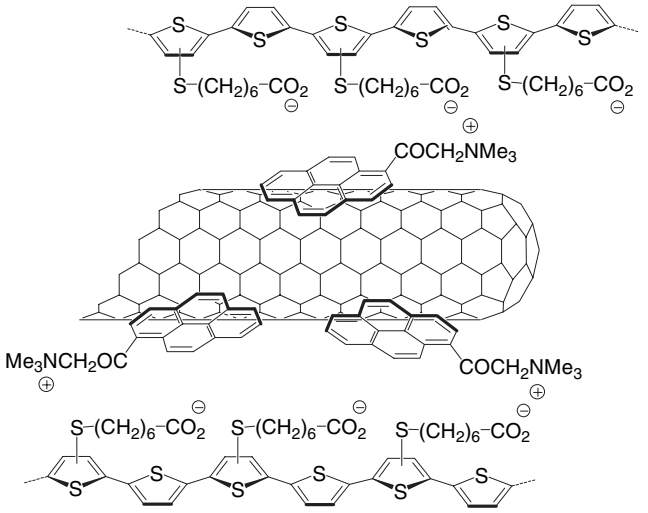


Figure 7. SWNT with positively charged pyrene and negatively charged polythiophene

rise to promising monochromatic solar energy conversion efficiencies up to 8.5% internal photoconversion efficiencies (IPCE).[20]

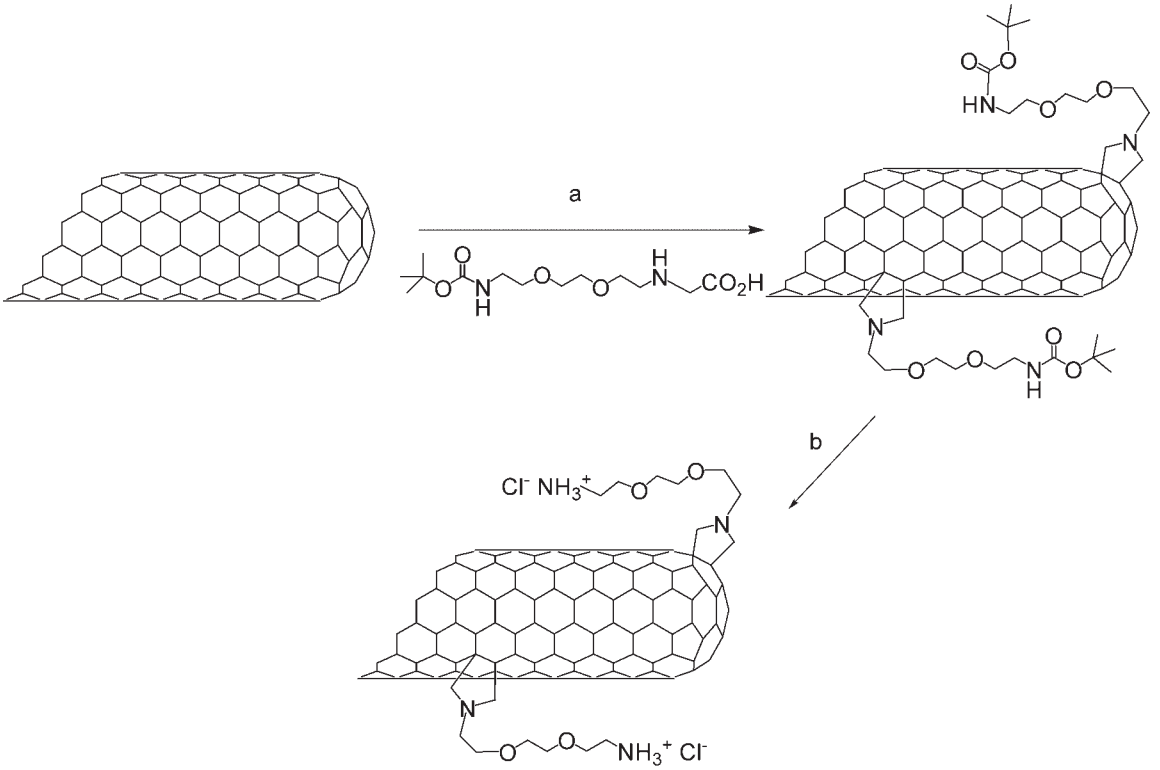
SWNT/pyrene$^+$ has also been used to immobilize polythiophene derivatives onto the SWNT surface (Fig. 7). Upon illumination, monochromatic incident photoconversion efficiencies between 1.2% and 9.3% were determined for single and eight sandwiched layers, respectively.[21]

BIOLOGICAL APPLICATION OF CARBON NANOTUBES

The 1,3-dipolar cycloaddition[22,23] developed in our group for the functionalization of C_{60} fullerene was successfully applied to the functionalization of NTs. Many aldehydes and amino acids can be used for the derivatization of NTs. We initially reported the synthesis of a few derivatives containing solubilizing alkyl or triethylene glycol chains on the nitrogen of the pyrrolidine and hydrogen or aromatic groups on α of the nitrogen.[24]

Dispersibility of NTs in aqueous media is a fundamental prerequisite to study their biological properties. NTs are practically insoluble in any type of solvent and only the recent development of strategies for linking chemical moieties to the tubes has facilitated their use.[14] With the aim to further functionalize the NTs, we designed a compound in which the ethylene glycol chain on the nitrogen of the pyrrolidine is terminated by a *tert*-butyloxycarbonyl (Boc) protected amino group (Scheme 2).[25] After removing the Boc by HCl, the NTs displayed a remarkably high solubility in water.

The amount of free amino functional groups per gram of material (loading) thus released, was measured using the quantitative Kaiser test. The results showed that amines were present between 0.30 to 0.50 mmol per gram. The presence of the free amino groups permits to link potentially any other molecular moiety. Water solubility opened the door to the use of NTs with biological species towards the



Scheme 2. (a) Paraformaldehyde, DMF, 120 °C. (b) HCl (gas), CH_2Cl_2, room temperature

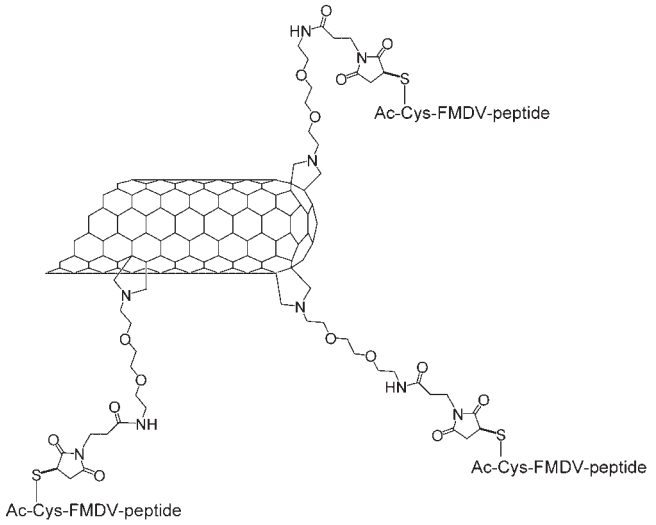


Figure 8. Nanotubes functionalized with the FMDV peptide

development of new delivery systems for therapeutic molecules.[7]

Peptide recognition

A first step to exploit NTs as vectors for drug, vaccine, or gene delivery was the observation of the molecular recognition of bioactive peptides covalently linked to NTs by specific antipeptide antibodies. A B-cell peptide epitope from the foot-and-mouth disease virus (FMDV), corresponding to the 141–159 region of the viral envelope protein VP1,[26] was introduced on the surface of the NTs by chemoselective ligation.[27] The free amino groups of SWNTs were first derivatized using a *N*-succinimidyl 3-maleimidopropionate. The *N*-terminal acetylated FMDV peptide, bearing a cysteine, was linked to the maleimido moiety on the wires, to obtain the peptide-SWNT conjugate (Fig. 8).

The antigenicity of the FMDV peptide-NTs was then proved by surface plasmon resonance analysis and enzyme-linked immunosorbent assay (ELISA).[27] The results from both experiments suggest that the peptide bound to the NT support adopts the correct secondary conformation necessary for recognition by specific antibodies. Moreover, a study *in vivo* showed that the FMDV peptide-NTs are also immunogenic. High antibody titers were obtained after immunization of mice, and the antibodies were able to neutralize the virus.[28] This result highlights the potential of functionalized NTs to transport vaccines based on synthetic peptides. However, NTs need to enter into the cells to deliver any linked molecule.

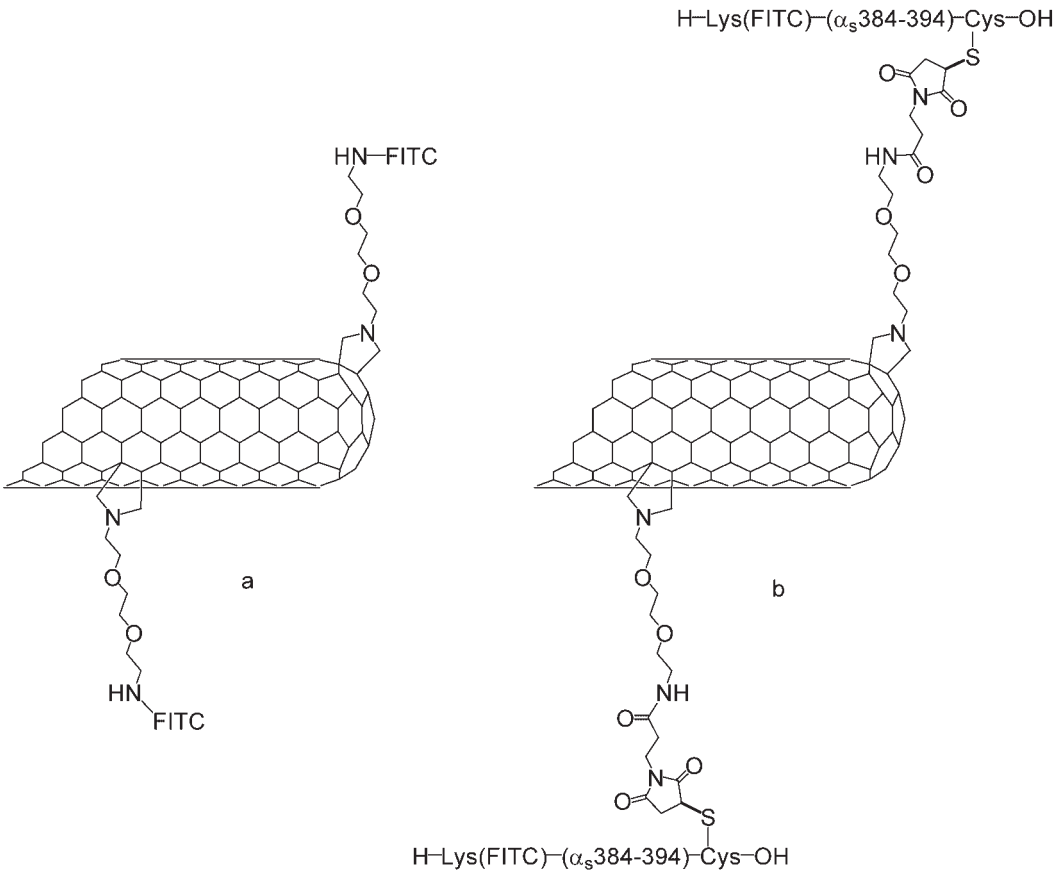


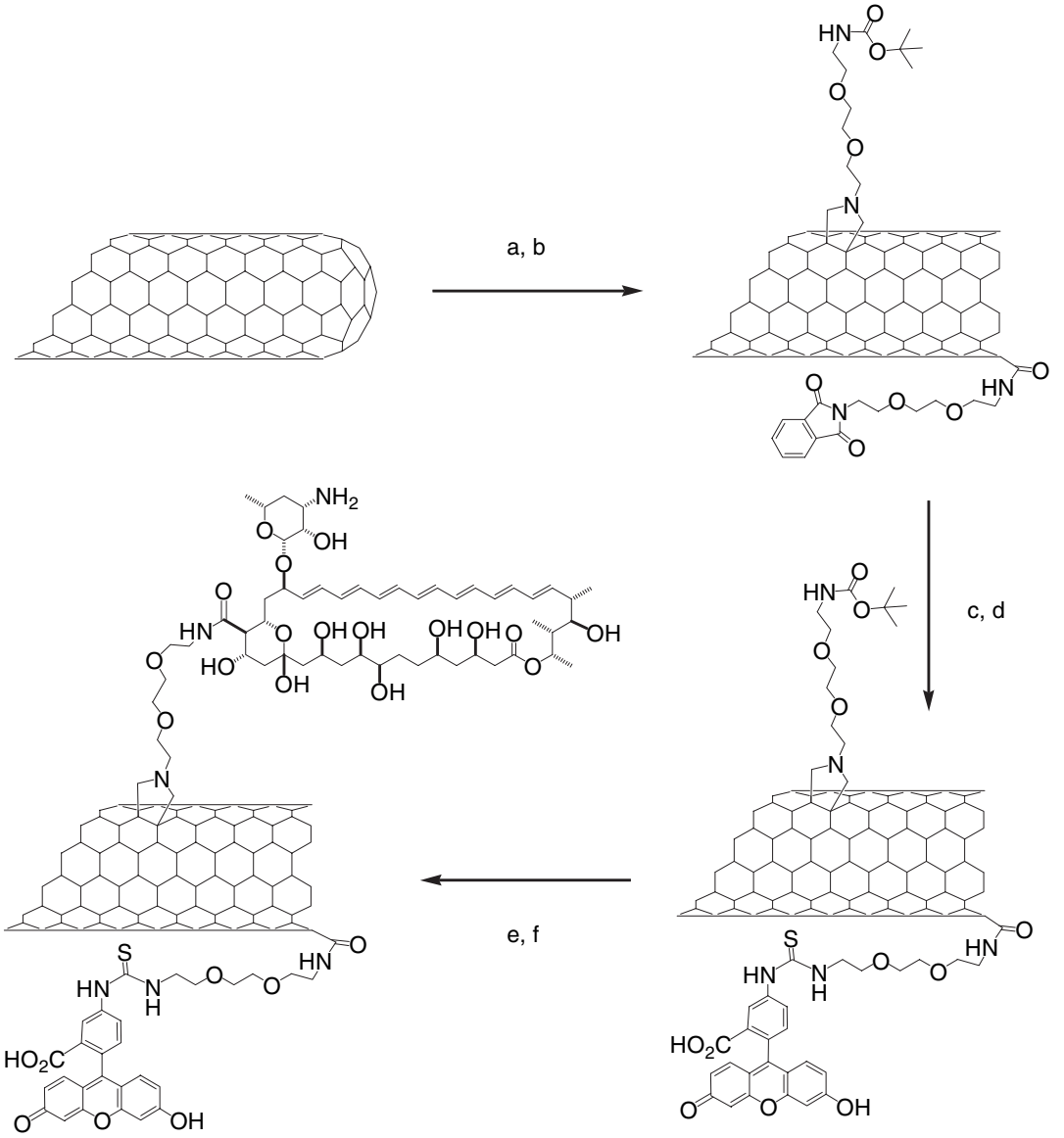
Figure 9. Nanotubes functionalized with (a) FITC, and (b) FITC-peptide 384-394 derived from the α-subunit of the protein G

Cell penetration ability

To determine whether NTs can be used to deliver active molecules into the cell, a FITC-labeled SWNT and a fluorescent peptide-SWNT conjugate were prepared (FITC, fluorescein isothiocyanate) (Fig. 9).[29]

The capacity of these NTs to penetrate into the cells was studied by epifluorescence and confocal microscopy on fibroblasts and HeLa cells cultured using RPMI medium at 37 °C. The confocal analysis clearly showed the presence of the labeled NTs inside the cells. In particular, the fluorescent peptide-NT conjugate was also able to cross the nuclear membranes and distribute into the nucleus. The translocation mechanism of functionalized NTs across the cell membrane is still not completely elucidated. This type of NTs is not uptaken by endocytosis since the internalization is not affected by temperature or the presence of endocytosis inhibitors. Indeed no difference in penetration capacity was observed between 37 and 4°C, and treating the cells with sodium azide.

The interaction of the functionalized NTs with cells was also studied by TEM. HeLa cells were incubated with ammonium SWNTs and MWNTs. The NTs were allowed to interact with the cells, which were then embedded into an epoxy resin. Ultrathin sections of the polymer were cut on an ultramicrotome with a diamond knife and examined by TEM. Many NTs were observed into the cytoplasm and the nucleus of the cells.[30] A careful analysis of the cell sections have also permitted to detect a NT in the process of crossing the plasma



Scheme 3. (a) Sonication in a HNO_3/H_2SO_4 mixture; neat $(COCl)_2$; Pht-N$(CH_2CH_2O)_2$-CH_2CH_2-NH_2 in dry THF at reflux. (b) Boc-NH$(CH_2CH_2O)_2$-CH_2CH_2-NHCH_2COOH/$(CH_2O)_n$ in DMF, 125 °C. (c) Hydrated NH_2-NH_2 in EtOH at reflux. (d) FITC in DMF. (e) HCl 4N in dioxane. (f) Fmoc-AmB, HOBt/EDC × HCl/DIEA in DMF; 25% piperidine in DMF

Table 1. Minimum inhibitory concentration (MIC) of the different NT conjugates

Conjugate	Minimum inhibitory concentration (MIC) [μg/mL]		
	Candida albicans (clinical isolate)	*Candida parapsilosis* ATCC 90118	*Cryptococcus neoformans* ATCC 90112
SWNT-$NH_3^+Cl^-$	>80	>80	>80
SWNT-AmB	13.8	1.6	0.8
MWNT-AmB	6.4	1.6	0.8
AmB	>80	20	5

The MIC corresponds to the lowest concentration of compound that inhibited visible growth of the organism.

barrier. NTs probably enter the cell by a passive mechanism in which they behave like nanoneedles and pass through the cell membrane without causing cell death. The same mechanism was also described by another group.[31]

Thus, the ability of NTs to penetrate into the cells can be exploited for delivery of different classes of therapeutic agents.

Enhancing drug delivery

NTs can be oxidized using strong oxidants giving rise to oxygenated functionalities at the tips and sidewalls. This opens a way to doubly functionalize the NTs with two different covalent approaches. Amphotericin B (AmB), which is considered to be the most effective antibiotic in the treatment of chronic fungal infections[32–34] was attached to NTs as well as FITC (Scheme 3).[35] AmB was covalently linked to ammonium-functionalized MWNTs and SWNTs. It is well known that AmB is highly toxic to mammalian cells.[34] One reason for this toxicity can be attributed to the formation of aggregates as a result of its lower solubility in water.[33] Conjugation of this drug to NTs revealed to have several advantages. Indeed, the evaluation of the antifungal activity of NTs, functionalized with AmB showed that the conjugated AmB is more potent than the free drug. The minimum inhibitory concentration (MIC) values were recorded against three species of fungi including *Candida parapsilosis*, *Cryptococcus neoformans*, and *Candida albicans* (Table 1). The maximal concentration used was 80 μg/mL. MWNT- and SWNT-AmB were highly effective. MIC was decreased of more than 12 times against for example *Candida albicans*.

This confirms that the activity of the drug is not prevented by its covalent binding to NTs. The fact that the activity of the drug is increased could be attributed to an improvement of AmB solubility in water or to the presence of multiple copies of AmB per NT molecule that might favor the interaction of the drug with the fungal membrane. To assess the biological properties of the functionalized NTs, the study of the toxicity effects of MWNT-AmB on mammalian cells were carried on. Jurkat cells were incubated with either MWNT-AmB or AmB as the control. Conjugation of AmB to NTs clearly reduces the toxic effects of the antimycotic on mammalian cells. At the highest doses, more than 40% of the cells died in the presence of AmB whereas all the cells remained alive upon treatment with MWNT-AmB. The results are very promising as they indicate that appropriate conjugation can increase the effectiveness of AmB while decreasing its toxicity on human cells. This approach can certainly be extended to other type of drugs.

Toxicity

Toxicity is an important parameter for all biological applications. It has been previously determined that as-produced NTs are toxic. From an NT exposure on human keratinocyte cells, oxidative stress and cellular toxicity were detected by the presence of free radicals, peroxidative products, antioxidant depletion, and loss of cell viability.[36] A study on MWNTs also showed their ability to induce irritation on epithelial cells.[37] However, it has been shown that cytotoxicity of water-soluble fullerene derivatives is a function of the degree of surface modification.[38] Thus, cytotoxicity caused by functionalized NTs was studied by flow cytometry.[29] This technique allows observation of the health status of the cell population by staining the cells with different markers. Various types of cells were incubated with increasing amount of fluorescent NTs. At concentration of 5 μM of NTs, 90% of the cell population remained alive. In contrast, increasing twice the concentration of tubes induced 80% of cell death. Moreover, no cytotoxicity was detected in the case of ammonium functionalized NTs up to doses of milligrams per milliliter.[30]

CONCLUSION

Covalent and supramolecular functionalizations of carbon nanotubes are the basic synthetic techniques to solubilize and use them in donor-acceptors systems or for drug delivery. The combination of NTs with various electron donors led to a new generation of donor-acceptor nanohybrids, which can be used for the development of carbon-based photovoltaic cells. Upon illumination these systems give rise to fast charge separations and slow charge recombinations. The first results are very

promising and further research in this field to obtain practical conversion of light energy into electricity is not only justified but also desirable.

We also demonstrated that carbon nanotubes are potentially powerful tools for biomedical applications. Surface modification of the NTs via 1,3-dipolar cycloaddition rendered them water soluble and further functionalization of the NTs with bioactive molecules hold great promise for application in drug, vaccine and gene delivery.

The chemical modification of carbon nanotubes is a little bit more than 5 years old and the NTs represent today a class of materials, which are expected to give rise to many applications. Future studies will determine the opportunities as well as the limitations of such materials.

Acknowledgements

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REFERENCES

1. Iijima S. *Nature* 1991; **354**: 56.
2. Iijima S, Ichihashi T. *Nature* 1993; **363**: 603.
3. Bethune DS, Kiang CH, DeVries MS, Gorman G, Savoy R, Beyers R. *Nature* 1993; **363**: 605.
4. Liu J, Rinzler AG, Dai H, Hafner JH, Bradley RK, Boul PJ, Lu A, Iverson T, Shelimov K, Huffman CB, Rodriguez-Marcias F, Shon Y-S, Lee TR, Colbert DT, Smalley RE. *Science* 1998; **280**: 1253.
5. Ziegler KJ, Gu Z, Peng H, Flor EL, Hauge RH, Smalley RE, *J. Am. Chem. Soc*. 2005; **127**: 1541.
6. Bianco A, Prato M. *Adv. Mater.* 2003; **15**: 1765.
7. Bianco A, Kostaleros K, Partidos CD, Prato M. *Chem. Commun*. 2005; 571.
8. Guldi DM, Rahman GMA, Zerbetto F, Prato M. *Acc. Chem. Res*. 2005; **38**: 871. DOI: 10.1021/ar040238I.
9. Hirsch A. *Angew. Chem. Int. Ed*. 2002; **41**: 1853.
10. Tasis D, Tagmatarchis N, Georgakilas V, Prato M. *Chem. Eur. J*. 2003; **9**: 4000.
11. Dyke CA, Tour JM. *Chem. Eur. J*. 2004; **10**: 812.
12. Banerjee S, Hemraj-Benny T, Wong SS. *Adv. Mater.* 2005; **17**: 17.
13. Nakashima N, Tomonari Y, Murakami H. *Chem. Lett*. 2002; 638.
14. Lin Y, Tailor S, Li H, Shiral Fernando KA, Qu L, Wang W, Gu L, Zhou B, Sun Y-P. *J. Mater. Chem*. 2004; **14**: 527.
15. Guldi DM, Rahman GMA, Jux N, Tagmatarchis N, Prato M. *Angew. Chem. Int. Ed*. 2004; **43**: 5526.
16. Guldi DM, Rahman GMA, Jux N, Balbinot D, Tagmatarchis N, Prato M. *Chem. Commun*. 2005; 2038.
17. Guldi DM, Rahman GMA, Jux N, Balbinot D, Hartnagel U, Tagmatarchis N, Prato M. *J. Am. Chem. Soc*. 2005; **127**: 9830.
18. Qin S, Qin D, Ford WT, Herrera JE, Resasco DE, Bachilo SM, Weisman RB. *Macromolecules* 2004; **37**: 3965.
19. Guldi DM, Rahman GMA, Ramey J, Marcaccio M, Paolucci D, Paolucci F, Qin S, Ford WT, Balbinot D, Jux N, Tagmatarchis N, Prato M. *Chem. Commun*. 2004; 2034.
20. Guldi DM, Rahman GMA, Prato M, Jux N, Qin S, Ford WT. *Angew. Chem. Int. Ed*. 2005; **44**: 2015.
21. Rahman GMA, Guldi DM, Cagnoli R, Mucci A, Schenetti L, Vaccari L, Prato M. *J. Am. Chem. Soc*. 2005; **127**: 10051.
22. Maggini M, Scorrano G, Prato M. *J. Am. Chem. Soc*. 1993; **115**: 9798.
23. Prato M, Maggini M. *Acc. Chem. Res*. 1998; **31**: 519.
24. Georgakilas V, Kordatos K, Prato M, Guldi DM, Holzinger M, Hirsch A. *J. Am. Chem. Soc*. 2002; **124**: 760.
25. Georgakilas V, Tagmatarchis N, Pantarotto D, Bianco A, Briand J-P, Prato M. *Chem. Commun*. 2002; 3050.
26. Rowlands DJ, Clarke BE, Carroll AR. *Nature* 1983; **306**: 694.
27. Pantarotto D, Partidos CD, Graff R, Hoebeke J, Briand J-P, Prato M, Bianco A. *J. Am. Chem. Soc*. 2003; **125**: 6160.
28. Pantarotto D, Partidos CD, Hoebeke J, Brown F, Kramer E, Briand J-P, Muller S, Prato M, Bianco A. *Chem. Biol*. 2003; **10**: 961.
29. Pantarotto D, Briand J-P, Prato M, Bianco A. *Chem. Commun*. 2004; 16.
30. Pantarotto D, Singh R, McCarthy D, Erhardt M, Briand J-P, Prato M, Kostarelos K, Bianco A. *Angew. Chem. Int. Ed*. 2004; **43**: 5242.
31. Cai D, Huang Z, Carnahan D, Mataraza JM, Chiles TC, Qin Z-H, Huang J, Kempa K, Ren Z. *Nat. Methods* 2005; **2**: 449.
32. Zumbuehl A, Carreira EM, Jeannerat D, Martin SE, Clark DD, Hussey SL, Peterson BR, Sohrmann M, Peter M, Stano P, Walde P, Vigassy T, Pretsch E. *Angew. Chem. Int. Ed*. 2004; **43**: 5181.
33. Szlinder-Richert J, Cybulska B, Grzybowska J, Borowski E, Bolard J. *Farmaco* 2004; **59**: 289.
34. Zotchev SB. *Curr. Med. Chem*. 2003; **10**: 211.
35. Wu W, Wieckowski S, Pastorin G, Benincasa M, Klumpp C, Briand J-P, Gennaro R, Prato M, Bianco A. *Angew. Chem. Int. Ed*. 2005; **44**: 6358.
36. Shvedova AA, Castranova V, Kisin ER, Schwegler-Berry D, Murray AR, Gandelsman VZ, Maynard A, Baron P. *J. Toxicol. Environ. Health A*. 2003; **66**: 1909.
37. Monteiro-Riviere NA, Inman AO, Riviere JE, Nemanich RJ, Wang YY. *Toxicol. Lett*. 2005; **155**: 377.
38. Sayes CM, Boyd AM, Sitharaman B, Wilson LJ, Colvin VL, Fortner JD, Lyon D, Guo W, Ausman KD, Tao YJ, West JL, Hughes JB. *Nano. Lett*. 2004; **4**: 1881.