Carbon nanotube–fluorenevinylene hybrids: Synthesis and photophysical properties

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ABSTRACT

Soluble, chromophore-functionalized carbon nanotubes (MWCNTs) have been synthesized via covalent approach with minimal alteration to the characteristic electronic states of MWCNTs. The key step includes incorporating a fluorenevinylene fluorescent moiety onto MWCNTs via the esterification of oxidized MWCNTs, where the solubility of the product is brought about by hexyl groups attached to the fluorene moiety. Electronic properties of the adduct were investigated by UV–Vis and luminescence spectroscopies, whereas its dispersability was monitored by SEM and TEM imaging. Fluorescence of the fluorenevinylene moiety is found to be quenched when bonded to the MWCNT sidewalls, indicating an electronic interaction in the excited state.

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1. Introduction

Carbon nanotubes (CNTs) have become one of the most interesting areas of research due to their novel structural, electronic and optical properties [1]. These outstanding properties have aroused great potential for implementing CNTs in molecular electronics applications [2]. In the recent years, attention has been directed to the preparation of donor–acceptor nanohybrids that are based on CNTs [3]. The general concept is that CNTs can accept electrons and then transport them under ballistic conditions along their axis [4]. Yet, it is still difficult to take their full advantages, since the pristine CNTs show some lack of solubility in any solvent.

In order to overcome this obstacle, CNTs can be chemically modified, either covalently or non-covalently, allowing enhanced dispersion in organic or aqueous media [5]. Moreover, chemical functionalization enables the efficient decoration of CNT sidewalls and tips with appropriate electron donors. On one hand, the non-covalent modification approaches have been used mainly in order to coat the CNT sidewalls with conjugated polymers and small organic dyes [6–16].

On the contrary, typical examples of chromophores attached covalently to both single-walled (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) include polyaromatic systems, such as pyrenes and porphyrins [17–31]. In most cases, SWCNTs and/or MWCNTs served as efficient electron acceptors that quench the luminescence of the grafted chromophore. The combination of an electron donor chromophore with an electron acceptor, the CNT nanostructure, is expected to result in the development of novel nanodevices that convert solar energy to electricity.

In the recent years, conjugated polymers have reached the role of a major, technologically important class of materials. They have the advantages of low cost and ease of modification of properties by appropriate substitution. Major applications include the development of polymer-based electronic devices such as field-effect transistors (FETs), solar cells and organic light-emitting diodes (OLEDs) [32,33]. In addition, oligomers are of significant interest due to their enhanced solubility in various media. In the recent years, the synthesis of various well defined conjugated oligomers derived from phenylene, fluorene, pyrrole and thiophene moieties has been achieved and reviewed extensively [33]. However, so far no report is associated with the synthesis and photophysical study of CNTs grafted with a conjugated oligomer. It would be of great interest to combine the exotic properties of CNTs with those of the conjugated oligomers. Such adducts can be incorporated into fluorenevinylene-based copolymers by condensation reactions yielding functional electroluminescent composites.

In this work we report on the preparation of a new dispersable CNT–fluorenevinylene hybrid through esterification reaction between oxidized MWCNTs and the hydroxylated chromophore (Fig. 1). Importantly, we complement our work with a detailed photophysical investigation on ground- and excited state CNT/chromophore interactions.

2. Materials and methods

All solvents and chemicals were reagent-grade quality, obtained commercially and used without further purification. The fluorenevinylene chromophore was chemically synthesized following a procedure reported elsewhere [34]. Briefly the diol, the chemical structure of which is shown in Fig. 1, was synthesized by Heck coupling of 9,9-dihexyl-2,7-divinylfluorene with 4-bromophenyl
acetate in a molar ratio 1:2. This reaction took place in triethylamine utilizing palladium acetate as catalyst. The reaction product was hydrolyzed in ethanol in the presence of a catalytic amount of aqueous solution of KOH. Finally, the diol was obtained by acidification with hydrochloric acid. In the present investigation, this diol was selected as chromophore because it is easier to prepare a symmetrical derivative compared to a non-symmetrical one. Moreover, this diol is very soluble in common organic solvents owing to the two hexyl chains. It is also strongly fluorescent due to the conjugated backbone. Multi-walled carbon nanotubes produced by the chemical vapor deposition method were obtained from Nanocyl (Belgium). The purity of the pristine material was approximately 95%.

The CNT sample was refluxed in concentrated HNO₃ for 48 h, to remove metal oxide particles remaining from the growth procedure. The mixture was then vacuum filtered through a 0.22 in Millipore polycarbonate membrane and subsequently washed with distilled water until the pH of the filtrate was ca. 7. The filtered solid was dried under vacuum for 12 h at 60°C. The purification protocol used here is known to add carboxylic groups to the nanotube edges and defects [35]. These materials will be referred as MWCNT–COOH. The introduction of the pendant fluorenevinylene chromophore groups was accomplished, starting from the MWCNT–COOH material. The synthetic route was the same employed by Haddon and co-workers to produce soluble SWCNTs containing alkyl esters as pendant groups [36].

Thus, 80 mg of MWCNT–COOH and 10 mL of thionyl chloride were mixed and stirred at 80°C for 24 h. The crude reaction mixture was then evaporated in vacuum to remove the excess of SOCl₂ and washed extensively with tetrahydrofuran (THF). In the following step, dried acyl-chloride modified CNTs were mixed with excess of diol in 5 ml of triethylamine. The resulting suspension was stirred for 24 h at 90°C. The product was isolated by centrifugation. The functionalized CNT material was redispersed in THF by bath sonication and was filtered off through a Teflon membrane with pore size 0.45 µm. The CNT adduct was washed extensively with THF to remove the excess of diol and dried in vacuum. This dispersion–filtration–washing protocol was repeated three times for more efficient purification of the functionalized tubes. In order to exclude non-covalent interactions between the organic moieties and the CNT sidewalls, we performed a blank experiment, in which HNO₃-treated MWCNTs were incubated in a solution of fluorenevinylene derivative in triethylamine. The complete chemical route containing all the modification steps is displayed in Fig. 1.

Raman spectra are measured with a ×50 objective at 785 nm excitation with a Renishaw micro-Raman spectrometer having 1800 grooves/mm grating and spectral resolution ~2 cm⁻¹. The data were recorded at the laser power of 0.4 mW, measured directly before the sample, in order to minimize heating effects. To avoid problems related to inhomogeneities in the samples all spectra were taken on four different spots for each sample. The phonon characteristics were obtained by fitting Lorentzian lineshapes to the experimental peaks, after background subtraction.

The UV–Vis-NIR absorption spectra of the CNT samples in THF were recorded on a Digilab Hitachi U-2800 spectrophotometer. The morphology of the CNT samples was revealed by Scanning and Transmission Electron Microscopy imaging. SEM images were recorded on a Leo 1530 FESEM Gemini scanning microscope. THF suspensions of MWCNTs were spin casted on mica substrates. All specimens were sputtered with gold. The TEM images were obtained from the casting of dispersions of modified CNTs in THF onto Nickel grids (with carbon layer coating, 200 mesh); these grids were analyzed with a Philips 208 electron microscope at a 100 kV voltage, and the resulting images were collected with an AMT high-resolution digital imaging camera. Thermogravimetric studies were performed on a TGA2950 (TA instruments) under nitrogen at 10°C/min in temperature range from 30 to 700°C.

Room temperature photoluminescence (PL) spectra were obtained with a Perkin Elmer LS45 luminescence spectrometer. The PL spectra were recorded by using an excitation wavelength of

Fig. 1. Synthetic scheme of MWCNT–fluorenevinylene hybrid.
400 nm. The PL dynamics has been studied with the time-resolved fluorescence upconversion technique using a mode-locked Ti:sapphire femtosecond laser (100 fs pulse duration, 80 MHz repetition rate) as the light source. The experimental set-up has been described in details previously [37,38]. Briefly, the second harmonic of the femtosecond laser at 400 nm, was used for the excitation of the samples. The excitation power was below 7 mW and the fluorescence decays were taken under magic angle conditions. For comparison, the decays of the MWCNTs–fluorenevinylene and the fluorenevinylene chromophore alone, in THF solutions, were detected. The solutions were put into a rotating cell in order to avoid heating. The fluorescence of the samples was collected and mixed with the delayed fundamental laser beam (gate) into a BBO crystal (type I) generating an upconversion ultraviolet beam. This beam passed through appropriate filters and a monochromator and it was detected through a photomultiplier as a function of the temporal delay between the fundamental laser beam and the fluorescence. The temporal resolution of the upconversion spectrometer was 160 fs.

3. Results and discussion

To introduce fluorenevinylene moieties to CNT sidewalls and tips, acyl-chloride modified carbon nanostructures were reacted with excess of diol under inert atmosphere to obtain soluble tubes by esterification reaction [36]. Excess diol was removed by centrifugation and repeating dispersion–filtration–washing cycles, as non-reacted substance simply adsorbed onto CNT sidewalls should not withstand such treatments.

MWCNT–fluorenevinylene adduct is soluble in common organic solvents such as tetrahydrofuran, chloroform and dichloromethane without precipitation for weeks. The solubility is estimated to be about 0.2 mg/ml in tetrahydrofuran. As a blank experiment, HNO₃-treated MWCNTs were incubated in a solution of fluorenevinylene derivative in triethylamine. After the isolation of the CNT material by extensive washing, we observed no dispersability of the tubes in tetrahydrofuran after prolonged bath sonication. In addition, TEM, Raman and TGA data give solid evidence that the fluorenevinylene derivative hardly adsorbs onto the CNT sidewalls (see below).

Observations by SEM and TEM imaging were performed to directly visualize the morphology of modified CNT material cast from THF solution. Typical images are presented in Figs. 2 and 3, respectively. Whereas MWCNT–COOH are typically aggregated in bundles (Fig. 2a), images of MWCNT–fluorenevinylene (Fig. 2b) reveal less bundled nanostructures than what is typically found for starting material.

This observation is consistent with MWCNT functionalization with the fluorenevinylene chromophore, where the conjugated functionality may disrupt the strong interactions between individual tubes. In addition, the TEM image of the hybrid material (Fig. 3) shows individually dispersed material. Concerning the dimension of the modified CNT external diameters, the majority of the tubes observed in the electron microscopy images have similar diameter when compared to the starting material (10–20 nm), since the size of the grafted chromophore is about 3 nm.

Additional evidence for the successful functionalization of MWCNT material is deduced by thermogravimetric analysis. Fig. 4 shows the thermal behavior of the starting MWCNT–COOH together with that of the hybrid material. As shown in a recent study of our group [35], the thermal degradation of nitric acid-treated MWCNTs is a multistage process (curve a). The first stage, up to a temperature of 150 °C, a weight loss is detected for the highly hydrophilic nitric acid-treated MWCNTs, which corresponds to the evaporation of the adsorbed water.

The second stage – from 150 to 350 °C – is attributed to the decarboxylation of the carboxylic groups present on the MWCNT walls. Thermal degradation in the range between 350 and 500 °C may be ascribed to the elimination of hydroxyl functionalities, attached to the MWCNT walls. Finally, at the temperatures higher than 500 °C, the observed degradation corresponds to the thermal oxidation of the remaining disordered carbon. The TGA curve of MWCNT–COOH exhibited a weight loss of 10% between 150 and...
500 °C, followed by a rapid weight loss of 12% up to 700 °C at which the amount of the MWCNT residue is about 72%.

The onset temperature for the thermal pyrolysis of parent diol is about 400 °C, whereas a residue of 40% is obtained at 700 °C (spectrum not shown) [34]. By assuming that at 700 °C the fluorenevinylene residues remaining in the hybrid material have the same wt.% as that of the neat diol, and the wt.% of oxygen-containing groups/disordered carbon is close to zero at this temperature, the wt.% of the fluorenevinylene moieties in the hybrid material (Fig. 4, curve b) may be roughly calculated and was found to be ~10%. Therefore, the chromophore/carbon ratio was calculated to be approximately 1:370. Analogous phenomena of relatively low functionalization degrees have also been observed by other groups [28]. The TGA profile of the blank experiment adduct (not shown) was almost identical with the one of MWCNT–COOH. This means that non-covalent interactions between the chromophore functions and the CNT sidewalls should be ruled out.

In order to confirm further the proposed functionalization scheme, UV–Vis–NIR absorption spectra were recorded at room temperature in THF solution. Fig. 5 shows the typical absorption spectra of free fluorenevinylene, oxidized MWCNTs and the functionalized material. The spectrum of free fluorenevinylene shows intense features in the range between 350 and 400 nm accompanied with an enhanced absorption for lower wavelengths. Interestingly, as it is evident from Fig. 5, in the spectrum of MWCNT–fluorenevinylene the absorption of the free molecule is superimposed on the rising background that originates from the presence of MWCNTs. Moreover, the characteristic double peaks in the range 350–370 nm of the free chromophore can hardly be resolved in the case of the composite material, possibly indicating weak electronic interactions of the fluorenevinylene and MWCNTs in the ground state.

Raman spectroscopy provides essential and useful information for the attachment of functional groups onto the surface of CNTs. The Raman spectra of MWCNT–COOH, hybrid adduct and material from the blank experiment excited with the 785 nm are illustrated in Fig. 6. For all the studied samples three characteristic bands, namely the D-band at ~1316 cm⁻¹, the G-band at ~1590 cm⁻¹ and the D'-band at ~1614 cm⁻¹ have been detected. The G-band originates from in-plane tangential stretching of the C–C bonds in graphene sheets, while the D and D' bands are disorder activated modes. It is well documented that an increase of the D-band intensity relative to the G one comprises a fingerprint for successful sidewall functionalization [39]. Upon functionalization, an increase of the D-band intensity relative to the G one is clearly observed. In the case of MWCNT–COOH and the material from the blank experiment, the D- to G- peak intensity ratio [I(D)/I(G)] were estimated to be 4.2 and 4.3, respectively. For the hybrid material the aforementioned ratio was determined to be about 5.2. This slight increase of the ratio may be connected to an efficient covalent functionalization through the esterification reaction.

Photoluminescence (PL) spectroscopy is a valuable tool for studying the interaction between the fluorenevinylene chromophore and MWCNTs in the excited state. In Fig. 7, the steady state fluorescence spectra of the fluorenevinylene moieties and MWCNT–fluorenevinylene composite material in THF solutions are depicted. The concentrations of both solutions have been adjusted to an optical density (O.D.) of 0.1 at 400 nm. The fluorenevinylene chromophore emits light in the blue spectral region with maximum at 447 nm exhibiting a quantum yield (Φ_F) of 55%. However, as it is evident from Fig. 7, a significant fluorescence quenching is observed for the composite samples (Φ_F = 2.5%) suggesting the presence of electronic interactions between the oligomer and the MWCNTs which can be identified as electron or energy transfer. In the inset of Fig. 7, the PL spectra are shown in normalized units. It is worth stressing that no significant differences were observed for the linewidth and

![Fig. 4. TGA profiles of MWCNT–COOH (curve a) and hybrid material (curve b).](image)

![Fig. 5. Absorption spectra of neat fluorenevinylene, MWCNT–COOH and hybrid material in THF solutions.](image)

![Fig. 6. Raman spectra of starting material MWCNT–COOH, hybrid adduct and material from the blank experiment, after background subtraction.](image)
peak position of the spectra in Fig. 7, indicating that the proposed functionalization scheme does not alter the chromophore architecture.

The PL dynamics of the MWCNT–fluorenevinylene composites, studied via the femtosecond upconversion technique, provides evidence for the electronic interactions between the fluorenevinylene and MWCNTs. Fig. 8a shows the PL decays of the fluorenevinylene and the MWCNT–fluorenevinylene composite in THF solutions. The concentration of the solutions has been adjusted to an O.D. of 0.7 at 400 nm. The excitation wavelength was 400 nm while the decay rate was monitored at 440 nm, which is close to PL maximum of fluorenevinylene chromophore.

As shown in Fig. 8a, the PL decay for the MWCNT–fluorenevinylene hybrid is overall faster than that of the chromophore moiety strongly indicating electronic interaction between the fluorenevinylene and the MWCNTs. More specifically, the PL decay of the composite is best fitted by a three-exponential decay function with an ultrafast component of 600 fs (15%), a fast component of 5 ps (25%) and a slow component of >300 ps (60%). On the other hand, the PL decay of the fluorenevinylene molecule is best fitted by a bi-exponential function with time constants of 5.3 ps (15%) and >300 ps (85%).

In the inset of Fig. 8a, the PL dynamics of the two samples is presented on a longer time scale where the slow decay component is evident. The ultrafast 600 fs component, existing only in the dynamics of the composite, is attributed to interactions between fluorenevinylene and MWCNTs. According to previous reports [40,41], the electron transfer from conjugated molecules to CNTs is an ultrafast process; faster than the energy transfer. Therefore, it is considered that the 600 fs component is due to a photoinduced electron transfer from the excited state of fluorenevinylene chromophores to MWCNTs. This is reminiscent of the behavior encountered in other covalently modified CNT/conjugated chromophore systems [25,42–46]. Using the results of the PL dynamics, a charge separation rate of $k_{cs} \approx 2 \times 10^{10}$ s$^{-1}$ has been calculated through the equation $k_{cs} = 1/(\tau_{hybr}) - 1/(\tau)$, where $\tau_{hybr}$ and $\tau$ are the amplitude averaged decay constants of the hybrid and the free fluorenevinylene, respectively. In a very recent work, Cordella et al. [46] have found extremely high charge separation rate ($5 \times 10^{10}$ s$^{-1}$) in an aminofluorene-functionalized SWCNT composite which was attributed to the large energy level displacement between the two moieties.

To determine whether the electronic interaction between the chromophores and the CNT sidewalls occurs within the same tube or through electron hopping from the chromophores to adjacent nanotubes, we have examined the PL decays of the MWCNT–fluorenevinylene composites for two different concentrations corresponding to O.D. of 0.7 and 1.4 at 400 nm excitation wavelength. The decay curves have been shifted for clarity and both are presented in Fig. 8b. As the concentration increases, more chromophores should be found in close proximity to nanotubes leading to faster decays if a hopping mechanism governs the dynamics. The observed similarity in PL decays for these two different concentrations strongly suggests that within the studied concentration range the electronic interaction occurs through the chemical bridge between the chromophores and the MWCNTs.

Finally, the 5 ps component found in both fluorenevinylene solution and composite material could be potentially attributed to vibronic or solvent relaxation while the slow decay component can be attributed to radiative population decay. The existence of these long decay components in the composite material is due to the fluorenevinylene units which do not interact with the nanotubes, thus exhibiting dynamics similar to the free chromophores.

Efficient charge separation in the chromophore-functionalized CNT composites is a prerequisite in developing CNTs based solar cells. Additionally, enhanced absorption throughout the visible spectrum and efficient transport of the carriers towards the electrodes are also needed. Due to their defect-free one dimensional structure, CNTs provide excellent channels for ballistic electron transport. Although promising results have been published [47], more systematic work has to be carried out to develop CNT-based organic solar cells.
4. Conclusions

Soluble, chromophore-functionalized MWCNTs have been synthesized through the covalent incorporation of a fluorenevinylene fluorescent moiety onto MWCNTs via the esterification of oxidatively etched MWCNTs. The MWCNT-fluorenevinylene composites are soluble in common organic solvents such as tetrahydrofuran, chloroform and dichloromethane without precipitation for weeks. TEM and SEM images have shown that the functionalized MWCNTs reveal less bundled nanostructures than the unfunctionalized MWCNTs meaning that the conjugated functionality disrupts the strong interactions between individual tubes. Raman spectroscopy has proved the chemical modification of the MWCNTs and has also indicated that the esterification reaction between MWCNT–COOH and the fluorenevinylene has occurred in a good extension. Efficient quenching of the fluorenevinylene PL in the composite accompanied by an ultrafast decay of the transient PL intensity of the composite indicates photoinduced electron transfer from the fluorenevinylene chromophore to the MWCNTs.

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