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Immobilization of Oligoquinoline Chains on Single-Wall Carbon Nanotubes and Their Optical Behavior

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ABSTRACT: Polymerization of vinylquinoline monomers onto properly modified single-wall carbon nanotubes (SWNT) using atom transfer radical polymerization (ATRP) conditions resulted in efficient grafting of optically active oligomeric chains onto the nanotubes. Two different carbon nanotube (CNT) modification procedures were used, resulting in amino- or hydroxy-functionalized CNTs, which were finally converted to active ATRP initiators. Polymerization of the vinylquinoline monomer resulted in highly soluble oligoquinoline-modified SWNTs. Characterization of these materials was performed using TGA, FT-IR, UV−vis, UV−vis−NIR, and photoluminescence spectroscopies. Immobilization of the quinoline units onto the nanotubes' surface greatly influences their optical behavior as shown explicitly for the case of the protonated analogues. Also, an electron transfer from the excited quinoline units to the SWNT was detected.

1. Introduction

Single-wall carbon nanotubes (SWNTs) have attracted considerable attention due to their extraordinary mechanical[1] and electronic properties.[2] The initial disadvantage of poor solubility has been overcame by various functionalization techniques[3] using either the covalent attachment[4] of different organic groups through reactions onto the π-conjugated backbone of the SWNTs or the noncovalent adsorption[5] or wrapping of various functional polymers.[6] "Grafting to"[7a] or "grafting from"[7b] techniques have been used for the modification of nanotubes employing conventional polymers. Furthermore, and in order to prevent the π-conjugation disruption, modifications[8] which allow the weak functionalization of the SWNTs and resulting in the lowest possible distortion of the electronic properties can be used. A combination of these approaches with the attachment of proper groups acting as atom transfer radical polymerization (ATRP) initiators[9] provides the possibility to control, to a certain extent, the degree of functionalization, allowing thus the grafting of polymeric chains of different length. Thus, ATRP initiators anchored to CNT's have been successfully used for the surface-initiated polymerization of various acrylates, styrene, and styrene-sulfonated sodium salts.[10,11] In cases where monomers with the desired functions are used, one can combine the electronic properties of SWNTs with the specific properties of the polymers selected for decoration, resulting in hybrid nanostructure materials.

From the materials scientist's point of view, a combination of a flexible semiconducting block containing a heteroatom-bearing monomer coupled to the nanotube surface is of special interest because of the optical behavior of the resulting materials. Since polyquinolines are one of the most promising classes of electron-transporting and electron-accepting polymers for use in various optoelectronic applications,[12] their combination with nanotubes is expected to provide a route for the modulation of their optical as well as their electronic properties. In such a case, processable materials where oligo- or polyquinolines will be covalently attached onto the SWNTs surface are expected to be potential candidates for various optoelectronic applications.

Keeping that in mind, we present facile routes toward the preparation of quinoline-functionalized SWNT materials (Scheme 1) and the detailed characterization of the resulting compounds using a variety of techniques, such as thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), UV−vis, and photoluminescence. Furthermore, optical characterization of the synthesized materials in DMF solution and upon protonation of the quinoline moiety was performed and has shown that the optical properties of the oligoquinoline chains grafted on the carbon nanotube are completely different from those of the polyquinoline homopolymers.

2. Experimental Section

2.1. Instrumentation and Measurements. Gel permeation chromatography (GPC) measurements were carried out using a polymer lab chromatographer with two Ultra Styragel linear columns (10^4, 500 Å), UV detector polystyrene standards and $CHCl_3$ as eluent, at 25 °C with a flow rate of 1 mL/min. The TGA experiments were performed on a TA Instruments Q50 series and a Setaram TGA instrument. The functionalization degree onto the nanotube surface was estimated according to (% carbon/atomic weight of carbon)/(% function group/molecular weight of the function group). For the detection of the UV−vis spectra, a Hewlett-Packard 8452A diode array was used. UV−vis−NIR spectra of the nanotubes derivatives were recorded on a Perkin-Elmer Lamba 900 spectrophotometer in SDS (9.7 mM) in D_2O. Continuous wave photoluminescence was measured on a Perkin-Elmer LS45 spectrofluorometer. The samples for the photoluminescence experiments were prepared as follows: for example, 2 mg of the SWNT-OQuin1 was dissolved in (i) 3 mL of DMF (0 acid volume fraction), (ii) 0.75 mL of formic acid/2.25 mL of DMF (0.25 acid volume fraction), (iii) 1.5 mL of formic acid/1.5 mL of DMF (0.5 acid

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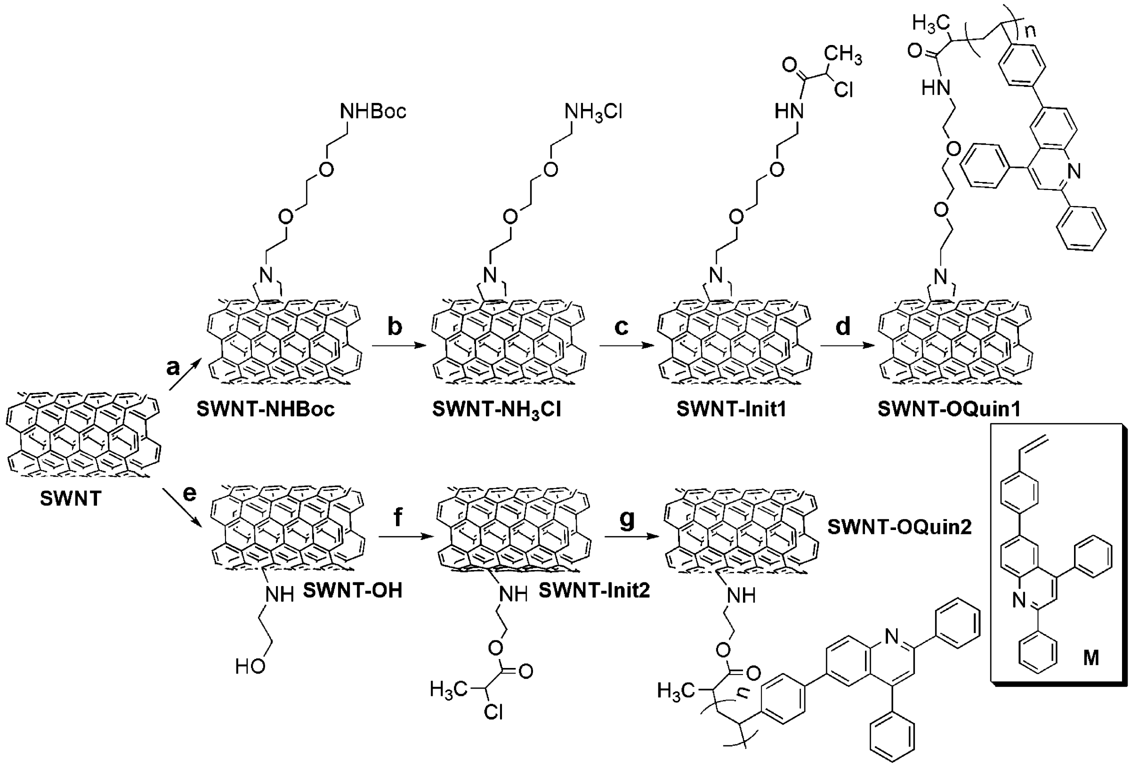
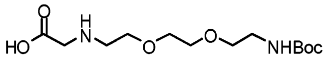
Scheme 1. Synthetic Routes toward the Preparation of Oligoquinoline Modified Single-Wall Carbon Nanotubes[a]



[a] Reagents and conditions : (a)  , paraformaldehyde, DMF, 120 °C, 5d; (b) HCl gas, DMF, room temperature, 1h; (c) 2-chloropropionyl chloride, triethylamine, DMF, 120 °C, 3d; (d) copper bromide, PMDETA, M, DMF, 110 °C, 18h; (e) 2-aminoethanol, DMF, 120 °C, 5d; (f) 2-chloropropionyl chloride, triethylamine, DMF, 120 °C, 3d; (g) copper bromide, PMDETA, monomer M, DMF, 110 °C, 18h.

volume fraction), (iv) 2.25 mL of formic acid/0.75 mL of DMF (0.75 acid volume fraction), and (v) 3 mL of formic acid (1 acid volume fraction). The transmission FT-IR spectra were recorded using a Nicolet Magna 850 spectrometer connected to a Nicolet Continuum FT-IR microscope by Spectra Tech Inc., equipped with an MCT/A detector. The magnification of both condenser and objective lenses was 15×. Each measurement was the accumulation of 128 scans at 2 cm^{-1} spectral resolution. The protonated sample for the FT-IR measurements was prepared as follows: 2 mg of the SWNT-OQuin1 was dissolved in formic acid (3 mL). Then, the solution was heated at 100 °C. When the formic acid was evaporated, the sample was further dried at 150 °C in high vacuum for 48 h.

2.2. Materials. The SWNTs used in this work were obtained from Carbon Nanotechnologies Inc. (HiPCO SWNTs) and NANOCYL S.A. (SWCNT 90+% C purity). The HiPCO SWNTs were used in the first synthetic route, while the NANOCYL SWNTs were used in the second synthetic route. Solvents and chemicals were purchased from Aldrich and were used as received, unless otherwise stated. The vinylquinoline monomer (M) and the quinoline homopolymer (PDPQ) (M_n = 9500 and PDI = 1.6 on the basis of the typical polystyrene equivalent gel permeation chromatography (GPC)) were synthesized based on a published procedure.[13a] SWNT-NH_3Cl was synthesized according to a recently reported procedures.[8]

Synthesis of SWNT-Init1. In a 100 mL round-bottom flask, equipped with a magnetic stirrer, 25 mg of SWNT−NH_3Cl was dispersed via sonication for 20 min in 25 mL of distilled DMF. The flask was cooled with an ice bath, and 1 μL (3.15 μmol) of distilled Et_3N and 2 μL (6.3 μmol) of 2-chloropropionyl chloride (CPC) were added. After 10 min of cooling the ice was removed, and the mixture was heated with oil bath at 120 °C for 3 days. After the mixture was cooled to room temperature, purification was achieved by passing the reaction solution through a 0.2 μm PTFE membrane. The obtained black solid was dispersed in 20 mL of DMF, sonicated for 15 min, and again filtered through a 0.2 μm PTFE membrane. The black solid was washed with DMF, THF, and diethyl ether. A black solid SWNT-Init1 (25 mg) was obtained after vacuum-drying for 24 h.

Synthesis of SWNT-OQuin1. To a round-bottom flask containing the SWNT-Init1 (12.5 mg; 0.473 μmol of initiator groups), distilled DMF (5 mL) was placed via a syringe, and the flask was sonicated for 5 min. The CuBr (0.473 μmol), pentamethyldiethylenetriamine (PMDETA) (0.473 μmol), and the vinylquinoline (M) (0.12 mmol) were added in the reaction flask, degassed, and refilled with argon four times. The reaction mixture was immersed in a thermostated oil bath at 110 °C for 18 h under an argon atmosphere. After the mixture was cooled to room temperature, purification was achieved by passing the reaction solution through a 0.2 μm PTFE membrane. The obtained black solid was diluted with 20 mL of DMF, sonicated for 15 min, filtered through a 0.2 μm PTFE membrane, and washed with methylene chloride, tetrahydrofuran, and diethyl ether in order to remove any unreacted monomer and copper complexes. The whole work-up was repeated five more times. A black solid SWNT-OQuin1 (30 mg) was obtained after vacuum-drying for 24 h.

Synthesis of SWNT-OH. To a round-bottom flask containing a magnetic stirrer, 50 mg of NANOSYL SWNT was dispersed in DMF upon sonication in an ultrasonic bath for 20 min. The flask was placed in oil bath at 120 °C, and then 3 mL (0.0498 mmol) of 2-aminoethanol was added. The reaction mixture was sonicated for 20 min every day for 5 days. After the mixture was cooled at room temperature, the black solid was filtered through a 0.2 μm PTFE membrane and washed with DMF several times to remove any

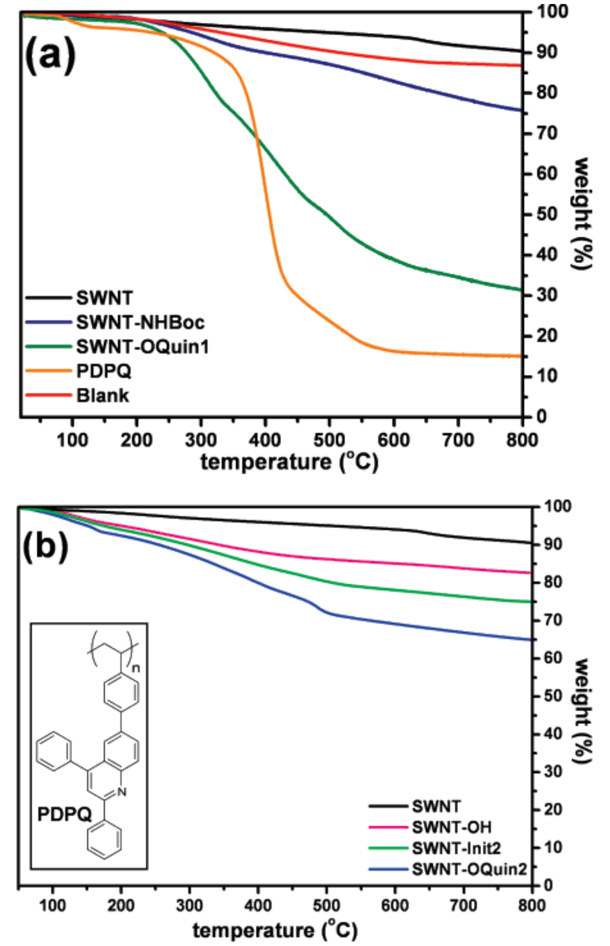


Figure 1. TGA thermogram of (a) single-wall carbon nanotube (HiPCO SWNT), the nanotube derivatives SWNT-Boc and SWNT-OQuin1, the PDPQ, and the blank experiment and (b) single-wall carbon nanotube (NANOCYL SWNT) and the nanotube derivatives SWNT-OH, SWNT-Init2, and SWNT-OQuin2 (10 °C/min under an argon atmosphere). In the inset, the chemical structure of the PDPQ is presented.

unreacted amine. The nanotubes were then dispersed in THF upon sonication, filtered through a 0.2 μm PTFE membrane, and washed with diethyl ether to obtain the final hydroxy-functionalized nanotubes (55 mg).

Synthesis of SWNT-Init2. In a 250 mL round-bottom flask with a magnetic stirrer, 50 mg of SWNT-OH was dispersed via sonication for 20 min in 100 mL of distilled DMF. The flask was cooled with an ice bath, and 1 mL (3.15 mmol) of distilled Et$_3$N and 2 mL (6.3 mmol) of CPC were added. After 10 min of cooling the ice was removed, and the mixture was heated with oil bath at 120 °C for 3 days. After the mixture was cooled to room temperature, purification was achieved by filtration the reaction mixture through a 0.2 μm PTFE membrane and washed with THF. The obtained black solid was dispersed in 20 mL of DMF, sonicated for 15 min, and filtered through a 0.2 μm PTFE membrane. The black solid was washed with DMF, THF, and diethyl ether in order to obtain (60 mg) of SWNT-Init2.

Synthesis of SWNT-OQuin2. To a round-bottom flask containing the SWNT-Init2 (25 mg, 83.05 μmol of initiator groups) distilled DMF (7.5 mL) was placed, and the flask was sonicated for 15 min. The CuBr (83.05 μmol), PMDETA (83.05 μmol), and the M (8.3 mmol) were added in the reaction flask, degassed, and refilled with argon four times. The reaction mixture was placed in a thermostated oil bath at 110 °C for 30 h under argon atmosphere. After the mixture was cooled at room temperature, the black solid was filtered through a 0.2 μm PTFE membrane and washed with DMF several times to remove any unreacted monomer. Then, the black solid was dispersed in DMF, sonicated, filtered through a 0.2 μm PTFE membrane, and washed several times with THF, chloroform, and diethyl ether. The SWNT-OQuin2 was dried at 50 °C, affording 30 mg of black solid.

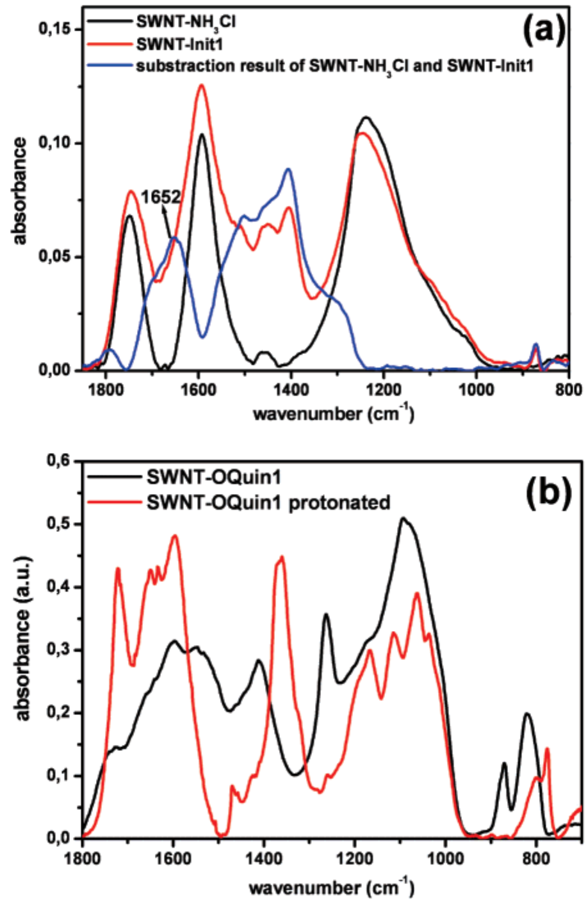


Figure 2. FT-IR spectra of (a) SWNT-NH$_3$Cl, SWNT-Init1, and the subtraction result of SWNT-NH$_3$Cl and SWNT-Init1 and (b) SWNT-OQuin1 and the protonated form of SWNT-OQuin1.

ATRP Using the SWNT and Monomer M (Blank). To a round-bottom flask containing the pristine NANOCYL SWNT (25 mg), distilled DMF (7.5 mL) was placed, and the flask was sonicated for 15 min. The CuBr (83.05 μmol), PMDETA (83.05 μmol), and the M (8.3 mmol) were added in the reaction flask, degassed, and refilled with argon four times. The reaction mixture was placed in a thermostated oil bath at 110 °C for 30 h under an argon atmosphere. After the mixture was cooled at room temperature, the black solid was filtered through a 0.2 μm PTFE membrane and washed with DMF several times to remove any unreacted monomer. Then, the solid was dispersed in DMF, sonicated, filtered through a 0.2 μm PTFE membrane, and washed several times with THF, chloroform, and diethyl ether. The compound was dried at 50 °C, affording 25 mg of black solid.

3. Results and Discussion

3.1. Synthesis. The oligoquinoline-functionalized SWNTs were prepared using two different synthetic routes (Scheme 1). In the first method, SWNT-NH$_3$Cl was synthesized based on a recent work reported by Prato et al.[8] TGA was initially employed in order to determine the degree of the functionalization onto the nanotube surface (Figure 1). The pristine SWNT and SWNT-NHBoc present a loss of weight of about 10% and 26% at 800 °C, respectively. This corresponds to the presence of one functional amino-terminated group per 120 carbon atoms.

The ATRP initiator was covalently attached to SWNT-NH$_3$Cl by an amide bond formation between 2-chloropropionyl chloride and the amine groups of SWNT-NH$_3$Cl in the presence of excess of triethylamine in DMF, providing the SWNT-Init1,

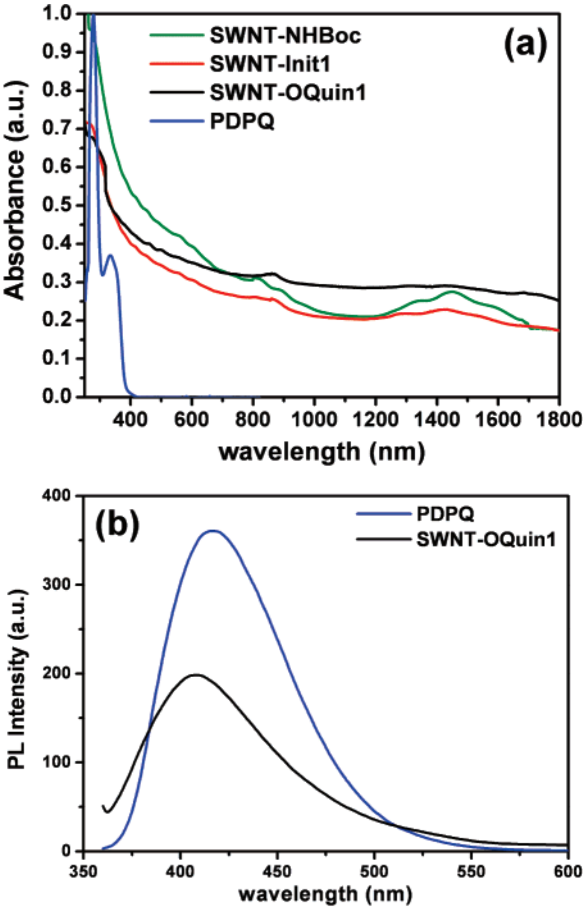


Figure 3. (a) UV−vis spectrum of PDPQ and UV−vis-NIR spectra of the nanotube derivatives: SWNT-NHBoc, SWNT-Init1, and SWNT-OQuin1 in SDS (9.7 mM) in D_2O. (b) Continuous wave photoluminescence spectra of PDPQ and SWNT-OQuin1 in DMF solution. Excitation wavelength at 340 nm.

as confirmed from the FT-IR spectra of Figure 2a. The subtraction result of the FT-IR spectrum of the SWNT-NH_3Cl and the SWNT-Init1 exhibit the appearance of a peak at 1652 cm^{-1}, assigned to the amide bond formation in the SWNT-Init1.

The growth of the oligoquinoline chains onto the SWNT was accomplished through the ATRP technique. The polymerization of the vinylquinoline monomer (M) with the ATRP technique, using different initiators[13a] and polythiophene macroinitiators,[13b] has been recently reported by our group. By employing similar ATRP conditions in this case, we succeeded in the polymerization of monomer M using the SWNT-Init1. The obtained materials are easily dispersible in common organic solvents like DMF and *o*-chlorobenzene (ODCB), while the homogeneous dispersions were kept more than 2 months without precipitating. The incorporation as well as the relative amount of the oligoquinoline chains can be estimated by comparison of the TGA traces of SWNT-NHBoc, SWNT-OQuin1, and poly(diphenylvinylquinoline) (PDPQ). Compounds SWNT-OQuin1 and PDPQ present a weight loss of about 59% and 85%, respectively, at 800 °C (Figure 1a). By a simple calculation, we estimate that 7−8 quinoline units have been incorporated in every functional group, assuming that all the initiator sites were reacting.

In the second synthetic route, the direct reaction of amino derivatives onto the carbon nanotube surface has been described in the literature[14] and is an easy method of providing functionalized carbon nanotube materials. Therefore, the reaction of pristine SWNTs in the presence of 2-aminoethanol in DMF led to the synthesis of SWNT-OH that has free hydroxyl groups in the periphery of the SWNT. Based on the TGA results of Figure 1b, the pristine SWNT and SWNT-OH present a loss of weight of about 9% and 17% at 800 °C, respectively. This corresponds to the presence of one functional hydroxy-terminated group per 58 carbon atoms and a functionalization percentage of 1.6%. The SWNT-Init2 was synthesized by an ester bond formation between 2-chloropropionyl chloride and the hydroxyl groups of SWNT-OH in the presence of excess of triethylamine in DMF, as confirmed from the TGA of Figure 1b. Assuming that all the hydroxyl groups of SWNT-OH were substituted with 2-chloropropionyl chloride, a weight loss of 29% at 800 °C was expected. However, the obtained weight loss of 24% of SWNT-Init2 shows that 77% of the hydroxyl groups of SWNT-OH were converted into ATRP initiator sites. Employing similar ATRP conditions as in the first synthetic procedure, we manage to decorate the surface of the SWNT with quinoline units. Also in this case, hybrid materials that are easily dispersible in common organic solvents, providing stable dispersible solutions were obtained. The incorporation of the quinoline moieties onto the SWNT-Init2 was 10%, which shows that not all the initiator sites were involved in this polymerization. In order to ensure that real atom transfer polymerization occurred under these conditions, a blank experiment was performed using unmodified SWNT. The resulting material was characterized by TGA as shown in Figure 1b. As is shown, only a minor difference was observed for this sample compared to the initial unmodified SWNT, which shows that no polymerization occurred in this case. This result is in full agreement with the recent literature where unmodified MWNT was used.[10a]

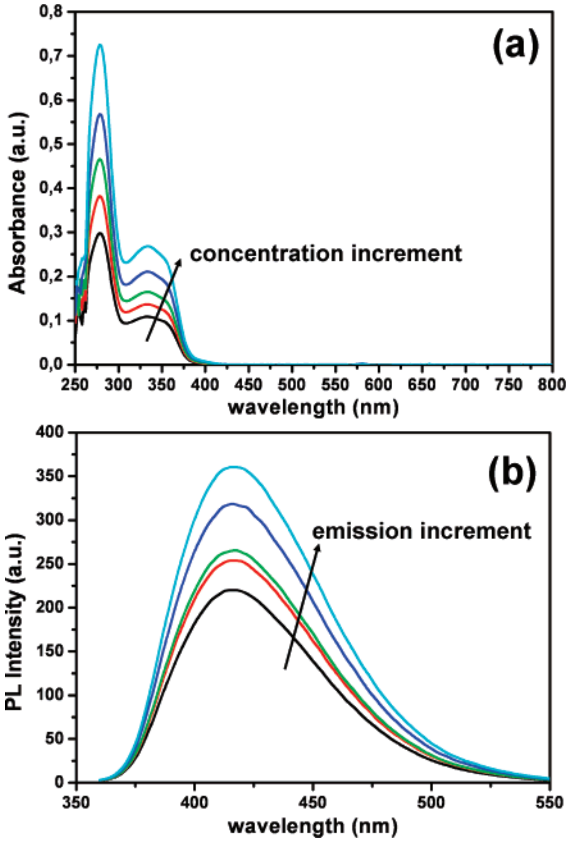


Figure 4. (a) UV−vis spectra and (b) continuous wave photoluminescence spectra of PDPQ at different concentrations. Excitation wavelength at 340 nm.

FT-IR characterization was used to verify the introduction of the quinoline units onto the SWNT surface. The spectrum of SWNT-OQuin1 shows additional peaks compared to SWNT-

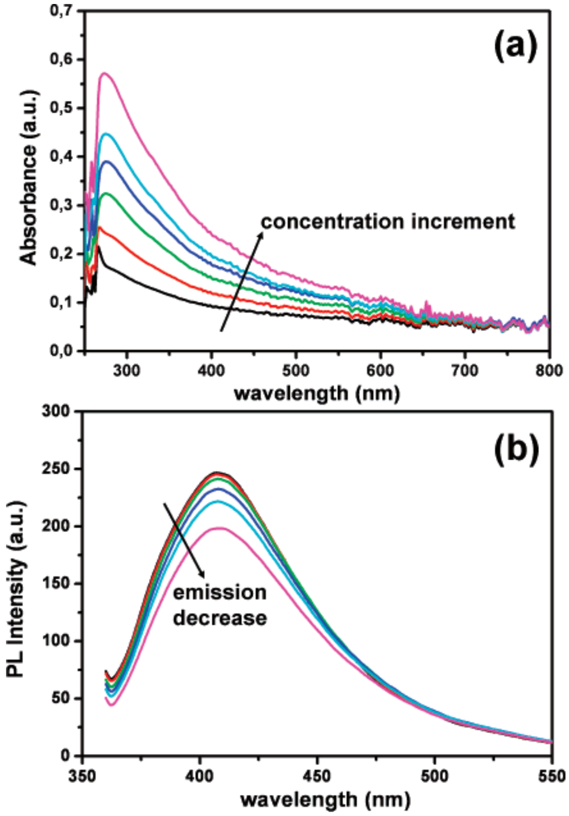


Figure 5. (a) UV−vis spectra and (b) continuous wave photoluminescence spectra of SWNT-OQuin1 at different concentrations. Excitation wavelength at 340 nm.

NH_3Cl, but more clearly the protonated oligoquinoline blocks on SWNT exhibit much better resolution (Figure 2b). Besides, the peaks at 1649 and 1633 cm^{-1} are assigned to the protonated quinolines, while the peaks at 1730 and 1350 cm^{-1} are attributed to the formic acid anions which are present as the counterions of the protonated quinoline.

3.2. Optical Properties. The optical properties of PDPQ and SWNT-OQuin1 are shown in Figure 3. The PDPQ exhibits two absorption maxima at 280 and 340 nm (Figure 3a) and emission maximum at 417 nm (Figure 3b). Comparing the UV−vis−NIR spectra of SWNT-NHBoc, SWNT-Init1, and SWNT-OQuin1, one can see that the spectra of SWNT-NHBoc and SWNT-Init1 are quite similar; it is not surprising since the only difference between the two nanotube derivatives is the replacement of the −Boc protective group by the chloropropanoyl amide initiator. The absorption spectrum of SWNT-OQuin1 presents a new shoulder between 300 and 400 nm which can be associated with the presence of the oligoquinoline on the nanotubes (Figure 3a). The presence of oligoquinoline is also corroborated by comparing the emission spectra of the SWNT-OQuin1 and PDPQ (Figure 3b). While no emission peak is observed at 417 nm upon excitation at 340 nm for compound SWNT-NH_3Cl and SWNT-Init1 in DMF solution, the appearance of an emission band at 407 nm (characteristic of the quinoline moieties), 10 nm blue-shifted though, after excitation at 340 nm of compound SWNT-OQuin1 in DMF solution, was clearly detected (Figure 3b), proving the presence of the quinoline units onto the carbon nanotubes.

Because of the attachment of the oligoquinoline chains onto the surface of the carbon nanotubes, the question of the optical or electronic coupling between them is arising. One evidence for the existence of such interaction is obtained from Figures 4 and 5, where the influence of the concentration increase on the emission peak is examined for quinoline units in the homopolymer (PDPQ) (Figure 4) and the modified SWNT-OQuin1 (Figure 5). So, concentration increment results in an increase of both the absorption and the emission peaks in the case of the PDPQ (Figure 4), while in the case of the immobilized chains (Figure 5), the intensity of the emission peak is decreasing, showing an electron transfer from the quinoline units to the nanotubes.

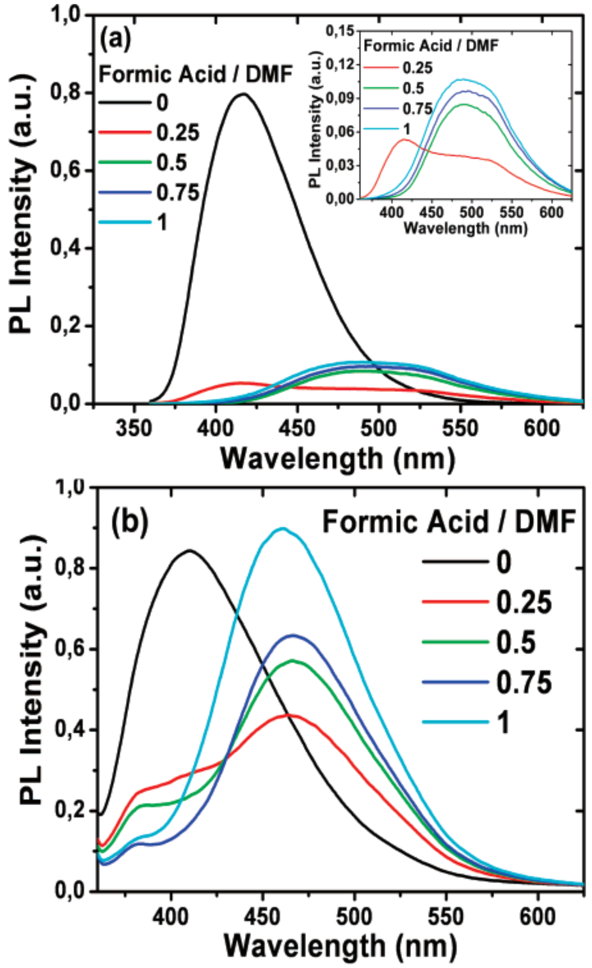


Figure 6. Continuous wave photoluminescence spectra of (a) PDPQ and (b) SWNT-OQuin1 at different volume fractions of formic acid/DMF mixture. Excitation wavelength at 340 nm. Inset: enlargement of the 350−650 nm area of (a).

As is known, polyquinolines are pH-sensitive due to the fact that protonation of the quinoline nitrogen atom shifts the emission spectrum.[12a] Furthermore, the red-shifted emission is greatly quenched due to the very strong tendency for excimer formation.[12a] This behavior is shown as a representative example in Figure 6a, where the emission maximum of PDPQ at different volume fractions of formic acid/DMF mixture is red-shifted from 417 to 493 nm, and at the same time the emission intensity is significantly reduced. Comparing the emission spectra of SWNT-OQuin1, at similar volume fractions of formic acid/DMF mixture as prepared for PDPQ, we observed the same emission maximum at 407 nm in DMF solution (Figure 6b), but upon protonation, this emission spectrum is red-shifted to a smaller extent (maximum at 464 nm instead of 493 nm), while surprisingly enough, in the case of SWNT-OQuin1 the peak retains its initial emission intensity. This shows that in this case the emission, originating from the protonated species, is not quenched most probably because the anchoring to the SWNT surface inhibits the excimer formation.

4. Conclusions

In summary, we herein demonstrate facile routes toward the preparation of an oligoquinoline-functionalized SWNT by ATRP conditions. Although, the ATRP technique has been employed in the past for the polymerization of vinyl monomers like styrene and various acrylates using modified carbon nanotubes acting as initiators, there was no report depicted in the literature for the polymerization of photoactive monomers (e.g., quinoline) with SWNTs. Moreover, the emission spectrum of SWNT-OQuin1 exhibits different optical behavior in contrast to the respective homopolymer PDPQ upon protonation. The excimer formation of polyquinolines is inhibited as was demonstrated in this work due to the immobilization of the quinoline units onto the nanotube surface. Finally, such hybrid materials will provide a way to combine the electronic properties of the SWNTs with those of the attached polymers, which in this case is the electron-accepting or the strong emission ability of the quinoline groups and examine their efficiencies into various optoelectronic applications.

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