Electronic Properties of Semiconducting Polymer-Functionalized Single Wall Carbon Nanotubes

Souzana N. Kourkouli†,‡,* Angeliki Siokou,†,* Andreas A. Stefopoulos,†,* Fotini Ravani,† Thomas Plocke,§ Matthias Müller,§ Janina Maultzsch,§ Christian Thomsen,§ Kostas Papagelis,†,* and Joannis K. Kallitsis†,§

†Foundation for Research and Technology Hellas, Institute of Chemical Engineering Sciences (FORTH-ICE-HT), Stadiou Str., Platani Achaias, 26504, Patras, Greece
‡Department of Chemistry, University of Patras, 26504, Patras, Greece
§Department of Materials Science, University of Patras, 26504, Patras, Greece

ABSTRACT: New hybrid materials were synthesized by functionalizing single wall carbon nanotubes (SWCNTs) with different semiconducting species. Vinyl quinoline monomers bearing electron accepting groups or even its ruthenium complex were used as organic semiconductors. UV–vis–NIR absorption spectroscopy, X-ray photoelectron spectroscopy and thermogravimetric analysis were used in order to qualify the resulted materials. Optical characteristics were studied by photoluminescence spectroscopy in neutral and acidic media. The electronic structure of the valence band and the surface electronic properties of the materials in the form of thin films developed on Si substrates were studied by ultraviolet photoelectron spectroscopy. Raman spectroscopy revealed the charge transfer mechanism between the polymer and the carbon nanotube while the recorded Raman resonance profiles showed significant changes in the transition energies and the widths of the resonance windows due to chemical modification of SWCNTs.

INTRODUCTION

Single wall carbon nanotubes (SWCNTs) have attracted much attention for the past decade as a material with interesting one-dimensional physics and potential applications in various fields.1 One of the promising applications of SWCNTs is in optoelectronics due to their excellent electron affinity, thermal conductivity, and mechanical strength and, of course, their chemical inertness2 due to the strong carbon–carbon bonds of the cylindrical graphitic lattice. The disadvantage of insolubility, mostly driven from the creation of bundles, has been overcome by functionalization of SWCNT surface using either covalent or noncovalent modifications. The chemical modification of SWCNTs has been extensively reviewed3,4 and provides a means for the combination of the dispersibility improvement with the introduction of an additional function that is dependent on the type of the groups used. “Grafting from” and “grafting to” constitute the two basic methods for the covalent attachment of polymeric chains to carbon nanotube’s surface.5 In the current work, the functionalization of SWCNTs with different semiconducting polymeric quinoline chains was occurred using the “grafting from” method. SWCNTs were properly modified to act as initiators for the atom transfer radical polymerization (ATRP) of quinoline monomers, affording the new hybrid materials.

In cases that the targeted application of the modified SWCNTs is their use as optoelectronic materials, attachment of semiconducting units is of utmost importance. Recent advances on the enrichment of the semiconducting character in SWCNTs5–8 expand the perspective for the use of such materials in photovoltaic applications.9–12 In these cases, the control over the electronic properties in the semiconducting SWCNTs is combined with the solubility improvement by simply using semiconducting organic species as covalent SWCNTs modifiers.13–17

Therefore, our approach mainly targets in the formation of new electron accepting materials and their combination with classical electron-donor functionalities producing polymer electron donor–acceptors directly applicable to plastic solar cells as the polymeric layer or as compatibilizers and stabilizers of the neat polymeric counterparts.16,19 In this case and in order to increase and ensure higher charge mobilities in the overall bulk phase, the incorporation of carbon based nanostructures, such as SWCNTs are highly desired.

The novel composite materials combine the unique properties of this type of semiconducting polymers20,21 with those of the SWCNTs22,23 giving rise to multifunctional systems with great potential. The main purpose of the current work is the detailed characterization of the obtained hybrid materials and...
the interactions between the SWCNTs and the semiconducting polymers. Working in this direction, different techniques like ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) were used for the study of the surface chemistry and electronic properties and UV–vis and Photoluminescence spectroscopy for the optical characterization. The successful modification of SWCNTs with the semiconducting polymers was confirmed by thermogravimetric analysis (TGA) and Raman spectroscopy. The combination of SWCNTs with semiconducting polymers offers an attractive route to reinforce the macromolecular compounds as well as to introduce novel electronic properties based on electronic interactions and/or morphological alterations between the two constituents.

**EXPERIMENTAL SECTION**

**Materials.** SWCNTs were purchased from Carbon Nanotechnologies Inc., Houston, TX (HiPCo form Unidym (lot no. P0261)). (2-Amino-5-bromophenyl) (phenyl) methane and 4-vinylphenylboronic acid were synthesized according to previous reports. 1-Bromo-4-nitrobenzene (Aldrich), 99%, p-cyanoacetophenone (Aldrich), methyl 2-pyridylketone (Aldrich), copper bromide 99.999% (Aldrich), N,N,N′,N′′,N′′′-pentamethyldiethylenetriamine 99% (Aldrich), 2-chloropropionyl chloride (Merck), ruthenium(III) chloride (Aldrich), 2,2′-bipyridyl 99% (Aldrich), lithium chloride (Aldrich), ammonium hexafluorophosphate >98% (Aldrich), and isopentyl nitrite (Fluka) were also used. All solvents were used without further purification unless otherwise stated. The filtration of SWCNTs was performed in a typical apparatus using filtration papers purchased from Sterlitech Corp., (Nylon-200 nm, 47 mm).

**Synthetic Procedures.** The synthetic routes of vinlylic monomers 6-(4-vinylphenyl)-2-cyano-4-phenylquinoline (MCNQ), 6-(4-vinylphenyl)-2-(2-pyridine)-4-phenylquinoline (MPyQ), ruthenium complex (MRuPyQ), and hybrid materials (SWCNT-CNQ, SWCNT-PyQ, SWCNT-RuPyQ) are described below.

**Vinlylic Monomer 6-(4-Vinylphenyl)-2-cyano-4-phenylquinoline.** A 50 mL round-bottom flask with 2-amino-5-bromophenyl (phenyl) methane (3g, 10.86 mmol), p-cyanoacetophenone (3.15g, 21.72 mmol), acetic acid (35 mL) and sulfuric acid 95% (0.1 mL) was degassed and stirred at 50 °C for 36 h. The reaction mixture was refluxed for 4 days. Cooling the reaction at room temperature resulting in the appearance of a light yellow solid that was vacuum-dried overnight resulting in 1.61g (76%).

**Vinlylic Monomer 6-(4-Vinylphenyl)-2-(2-pyridine)-4-phenylquinoline.** A 50 mL round-bottom flask with 2-amino-5-bromophenyl (phenyl) methane (3g, 10.86 mmol), acetylpyridine (2.631 g, 21.72 mmol), acetic acid (35 mL), and sulfuric acid 95% (0.1 mL) was degassed and filled with argon. The reaction mixture was refluxed for 3 days. After cooling the solution, a light brown cotton like solid appeared. Purification was achieved after filtration in a Por 3 filter and the solid was washed with pure methanol. The white solid (6-bromo-2-(2-pyridine)-4-phenylquinoline (BrPyQ)) was vacuum-dried overnight resulting in 2.7 g (80%).

**Vinlylic Monomer 6-(4-Vinylphenyl)-2-(2-pyridine)-4-phenylquinoline.** A 50 mL round-bottom flask with 2-amino-5-bromophenyl (phenyl) methane (3g, 10.86 mmol), acetylpyridine (2.631 g, 21.72 mmol), acetic acid (35 mL), and sulfuric acid 95% (0.1 mL) was degassed and filled with argon. The reaction mixture was refluxed for 3 days. After cooling the solution, a light brown cotton like solid appeared. Purification was achieved after filtration in a Por 3 filter and the solid was washed with pure methanol. The white solid (6-bromo-2-(2-pyridine)-4-phenylquinoline (BrPyQ)) was vacuum-dried overnight resulting in 3.37 g (86%) yield. Into a 100 mL round-bottom flask BrPyQ (2g, 5.54 mmol) was added 4-vinylphenylboronic (1g, 6.65 mmol), K2CO3, 2 M solution (8.3 mL), Pd(PPh3)4 (0.2 g, 0.166 mmol), and toluene (50 mL). The flask was degassed and filled with argon. The reaction mixture was refluxed for 4 days. Then the mixture was filtered from paper filter followed by the extraction of the organic layer with ethyl acetate (3x 40 mL) and distilled water (3x 40 mL). The organic part was dried with MgSO4 and after filtration the solution was evaporated at reduced pressure in rotary evaporator resulting yellow solid. This was dried and then dispersed in methanol for further purification. The solid was then filtered from Por 3 and the light yellow solid was vacuum-dried overnight resulting in 1.61g (76%).

**Synthesis of Hydroxy-Functionalized SWCNTs (SWCNT-OH).** A 20 mL round-bottom flask with SWCNTs (100 mg, 8.33 mequiv C), p-aminophenol (1 g, 9.17 mmol) and isopentyl nitrile (3 mL), was degassed and filled with argon reacting at 65 °C for 36 h. Filtration of the black solid, from Nylon-200 nm membrane, and continuous wash with acetone was made until a colorless filtrate was obtained. Then the solid was dispersed in dimethylformamide (DMF) (100 mL) and stirred at 50 °C for additional purification. Again, filtration from same type membrane resulted in a black solid, which was vacuum-dried overnight at 75 °C.

**Synthesis of ATRP Initiator Groups onto SWCNTs (SWCNT-Init).** A 100 mL round-bottom flask with SWCNT–OH (50 mg), chloropropionyl chloride (CPC) (3 mL, 30 mmol), dry triethylamine (4 mL, 31.2 mmol), and distilled DMF (60 mL) was degassed, filled with argon, and placed in the ultrasonic bath for 20 min. The reaction mixture was stirred at 100 °C for 2 days. Filtration of the black solid from Nylon-200 nm membrane and continuous wash with acetone and distilled dichloromethane until colorless filtrate was made. Then the solid was dispersed in DMF (100 mL) and stirred at 50 °C for additional purification. Again, filtration from same type membrane resulted in a black solid, which was vacuum-dried overnight at 75 °C.

**Polymerization of Quinoline Monomers onto SWCNTs (SWCNT-CNQ, SWCNT-PyQ, SWCNT-RuPyQ).** A 5 mL round-bottom flask with SWCNT-Init (20 mg), CuBr (10 mg, 0.07 mmol), and PMDETA (15 μL, 0.07 mmol) was degassed and filled with argon. Distilled DMF and the respective monomer (MCNQ, MPyQ, MRuPyQ) (1 mmol) were added with a syringe, and then the flask was placed in the ultrasonic bath for 20 min. The reaction mixture was stirred at 90 °C for 1 day. Then the mixture was dissolved in chloroform and the suspension was filtered from Nylon-200 nm membrane for purification from any unreacted monomers. Then the solid was dispersed in DMF (100 mL) and stirred at 50 °C for additional purification. Again, filtration from same type membrane resulted black solid which was vacuum-dried overnight at 75 °C.

**Instruments and Measurements.** The structures of the synthesized materials were clarified by 1H NMR spectroscopy with a Bruker Avance DPX 400 MHz spectrometer. 

Centrifugation was made using a Hettich Zentrifugen, Universal 3200, and sonication was done on a Bransonic (Branson), ultrasonic cleaner 2510 model.

TGA experiments were performed on a TA Instruments Q50 series. The functionalization degree of functionalized SWCNTs was estimated according to: (% carbon/atomic weight of carbon)/(% carbon/atomic weight of carbon).
The high and low energy cutoff (HOMO) can only be measured directly by using inverse photoemission, or it can be deduced from ionization energies, work function and other UPS-spectra cutoff features where the error margin is significant, due to the process of fitting straight lines. The ionization potential (IP) of the material under investigation, i.e., the distance between the vacuum level and the HOMO cutoff, is calculated by adding the absolute values for the measured work function and the HOMO cutoff. The position of the lowest unoccupied molecular orbital (LUMO) can only be measured directly by inverse photoemission, or it can be deduced from HOMO–LUMO energy gap measurements.

The unmonochromatized MgKα (1253.6 eV) line was used for the UPS measurements. The analyzer was working at constant pass energy (E_p = 36 eV) which giving a full width at half-maximum of the main C 1s UPS peak of 1.4 eV. The UPS core level spectra were analyzed using a fitting routine, which can decompose each spectrum into individual mixed Gaussian–Lorentzian peaks after a Shirley background subtraction. Regarding the measurement errors, for the XPS core level peaks we estimate that for a good signal-to-noise ratio, errors in peak positions are of about ±0.05 eV.

**RESULTS AND DISCUSSION**

The synthesis of monomers was performed according to our previously described methodology, and characterized accordingly. The vinyl quinoline pyridine ruthenium complex was obtained by complexation of the vinylpyridine quinoline using cis-tripyridinerruthenium chloride in ether. SWCNTs were properly modified by the subsequent attachment of phenolic and isopropyl chloride groups that can act as initiator for the...
atom transfer radical polymerization\textsuperscript{29} of the vinyl quinoline monomers. The obtained monomers and hybrid materials are presented in Chart 1.

The final hybrid materials were characterized first with TGA and the results proved, in all cases, the attachment of the quinolines on the nanotubes surface (Figure 1). For SWCNT-CNQ and SWCNT-PyQ almost the same amount of quinolines was immobilized on the SWCNTs, about 11\%, while for the SWCNT-RuPyQ an enhancement of the weight loss (∼27\%) is observed. The homopolymers PCNQ and PPYQ indicate a single degradation state about 400 °C which is in accordance with that of the hybrid materials.

The optical characterization of the homopolymers (PPyQ and PCNQ) and the obtained hybrid materials (SWCNT-CNQ, SWCNT-PyQ, SWCNT-RuPyQ) dispersed in DMF and formic acid (F.A.) was performed with UV−vis, UV−vis−NIR absorption spectroscopy (Figures 2, parts a and b, and 4) and photoluminescence spectroscopy (Figures 3, 4). From the UV−vis spectra and based on the well-known relation between the band gap energy ($E_\text{g}$) and the cut off wavelength ($\lambda_c$), $E_\text{g} = h^*c/\lambda_c$ ($h$ is Planck's constant and $c$ is the speed of light), we were able to estimate the band gap energy of the homopolymers and the derived hybrid materials. The calculated values for the SWCNT-CNQ, SWCNT-PyQ and SWCNT-RuPyQ materials were 2.8(±0.1) eV, 2.8(±0.1) eV and 2.9(±0.1) eV, respectively. Comparing with those of the corresponding homopolymers PCNQ, 3.2(±0.1) eV and PPYQ, 3.3(±0.1) eV, the band gap energies of the obtained hybrid materials are much lower mainly due to the new energy states introduced by the SWCNTs.

Polyquinolines are pH-responsive due to the protonation of the quinoline nitrogen atom which red shifts the emission spectrum. This is shown in Figure 3 where the emission spectra of hybrid materials (SWCNT-CNQ, SWCNT-PyQ) dispersed in formic acid show an electron transfer from the quinoline units to the SWCNTs. In addition, the emission spectra of the protonated hybrid materials do not show the quenching normally observed on the polymeric quinolines after protonation due to their immobilization on the SWNT surface, and the absence of excimer formation.\textsuperscript{20,21}

From Figure 5, it is evident that the relative integrated intensities of the D to G' band ($I_D/I_{G'}$) increases dramatically upon functionalization. The extracted $I_D/I_{G'}$ values for pristine and functionalized materials are presented in Table 1. Alternatively, Maultzsch et al.\textsuperscript{32} argue that the G-band itself can be defect induced and suggest that the intensity of the D band should be normalized to the intensity of the second order mode 2D as a measure for defect concentration in SWCNTs. The corresponding ratios are also included in Table 1.

The inset of Figure 5 shows the Raman spectra of the studied materials in the radial breathing mode (RBM) frequency region, at 785 nm excitation. The spectra were normalized to the intensity of the G-band. At this laser wavelength the excitation is primary resonant with $v_2 \rightarrow c_2$ transitions of
semiconducting nanotubes. The members of two branches, namely the (12,1) and the (11,0) contribute to the spectra.33

The highest intensity RBM feature at 267 cm$^{-1}$ corresponds to a diameter of 0.862 nm and can be assigned to (10,2) or (11,0) nanotubes of the (11,0) branch. Interestingly, the decorated compounds exhibit a significant reduction of the Raman scattering intensity for the (12,1) branch, located at the region between 210 and 240 cm$^{-1}$.

The energy shift of the G-Mode of the samples SWCNT-CNQ, SWCNT-PyQ, and SWCNT-RuPyQ compared to the starting material (black) at an excitation wavelength of 514 nm.
Comparing the G mode positions of the tubes decorated with RuPyQ had a red shift of the high energy mode 2.5 eV, respectively, compared to the starting material while SWCNT-CNQ and SWCNT-PyQ showed a blue shift of 4.5 eV for the pristine SWCNTs. On the left side, a detailed view of the area around the Fermi level.

For the charging of the tubes due to the ruthenium ion, two concepts are competing: the first is a charging via the whole polymer chain, as it were “by wire”. The second and more likely concept takes into account the small distances between each ion and the tube surface because of the typical polymer wrapping. This means that lots of ions come very close to the nanotube surface, the architecture of the metal complex may be considered to be low.

For the charging of the tubes due to the ruthenium ion, two concepts are competing: the first is a charging via the whole polymer chain, as it were “by wire”. The second and more likely concept takes into account the small distances between each ion and the tube surface because of the typical polymer wrapping. This means that lots of ions come very close to the nanotube surface, the architecture of the metal complex may even allow a direct contact between them. Because the polymers are semiconducting their conductivity is supposed to be low.

For the charging of the tubes due to the ruthenium ion, two concepts are competing: the first is a charging via the whole polymer chain, as it were “by wire”. The second and more likely concept takes into account the small distances between each ion and the tube surface because of the typical polymer wrapping. This means that lots of ions come very close to the nanotube surface, the architecture of the metal complex may even allow a direct contact between them. Because the polymers are semiconducting their conductivity is supposed to be low.

Additionally full resonance profiles of the different samples and tubes were recorded (Figure 6). A CaF$_2$ crystal was used for normalization of the intensities of the RBM signal for the different excitation wavelengths. The transition energies of all our samples are shifted about 30–60 meV to lower energies as compared to the starting material. Only the SWCNT-PyQ sample shows an increased full half-width. The shift of the transition energy originates from the charge transfer, which is causing a doping effect in the SWCNTs. Because of the doping effect new acceptor or donor levels develop in the SWCNTs, decreasing the effective band gap.

The XPS and UPS techniques were also used for a more thorough characterization of the SWCNTs attached groups as well as the influence of the various groups attached on the electronic levels of the hybrid materials. Apart from the hybrid materials, the pristine SWCNTs and the monomer MCNQ were studied for comparison purposes.
The C1s peaks originating from the two starting materials i.e. the pristine SWCNTs sample and the quinoline monomer (MCNQ) are shown at the bottom and the top of Figure 7 respectively. The spectrum of the pristine nanotubes can be analyzed into four components. The main one at BE= 284.2 eV corresponds to carbon atoms in the sp² bonds of the graphitic structure while the one shifted by +1 eV from the main peak corresponds to C−Cs p3 bonds. This peak is always apparent in the C1s spectra of SWCNTs and it is attributed to the presence of carbon in defect sites such as rings along with defects on the nanotube walls, vacancies, heptagon-pentagon pairs, kinks as well as carbon atoms at the edges of the graphitic planes. The peaks at 286.8 and 288.8 eV are attributed to carbon atoms attached to oxygen containing functionalities in the form of C−O(H) and O−C═O respectively. Finally the peak close to 291 eV is a characteristic loss feature of the C1s spectrum of graphitic carbon and represents the energy loss of C1s electrons due to π−π* transitions that occur during to photoionization procedure. The main C1s component of the quinoline monomer appears at 285 eV. The peak at 286.6 eV is attributed to carbon atoms bonded to nitrogen in pyridinic (C═N−C) and cyano (−C≡N) bonds, while the one at and at 287.8 eV is attributed to carbon atoms in −C==O (carbonyl) or O−C═O or O==C−N bonds (dihydroxy, dialkoxy, amide).

All these components appear also at the C 1s spectrum of the quinoline modified SWCNTs sample (second from the bottom in Figure 7) where the contribution from the graphitic body of the SWCNTs has been considerably suppressed. The N1s spectrum of the quinoline monomer is quite noisy and appears to have a wide peak (fwhm = 3 eV) at binding energy 400.3 eV. This peak corresponds to N atoms in cyano (−C≡N) units while the peak originating from nitrogen atoms in the pyridine bonds, which should appear at slightly higher binding energy is not discernible probably due to the poor quality of the spectrum. The N1s spectrum of the quinoline modified SWCNTs has the same features.

Next, the valence band structures of the materials were investigated by UPS (Figure 8). The prominent peak of the SWCNTs valence band, which extends up to the Fermi edge cutoff, is observed at a binding energy of 3 eV and it is attributed to C2pπ states, as reported in previous studies. The low-binding-energy region of the monomer CNQ film appears to have a strong feature at about 5 eV caused by the N lone pair electrons which contribute to the π-system. This feature becomes less sharp at the hybrid material while the SWCNT-PyQ and SWCNT-RuPyQ hybrids have their density of states close to the Fermi level significantly suppressed. This is better shown on the left side of Figure 8 where a more detailed view near the low-binding-energy region is presented. The HOMO cutoff (valence band edge) positions for the modified nanotubes are measured at 1.3 ± 0.05 eV for SWCNT-CNQ, 1.8 ± 0.05 eV for SWCNT-PyQ and 2.2 ± 0.05 eV for SWCNT-RuPyQ.

The work function (eΦ) for each material is derived from the high binding energy cutoff of the UPS spectra and its value for the SWCNTs is 4.3 ± 0.1 eV in agreement with reported values. The eΦ values for the modified nanotubes are reduced to 3.7 ± 0.1 eV, 3.5 ± 0.1 eV and 3.4 ± 0.1 eV for SWCNT-CNQ, SWCNT-PyQ, and SWCNT-RuPyQ respectively indicating that electron transfer take place in all three cases toward the carbon nanotubes leading to a work function decrease.

The ionization potential, i.e., the HOMO position from the vacuum level, can be found by adding the HOMO cutoff energy (distance between the valence band edge and the Fermi level) to the work function (distance between the Fermi level and the vacuum level).
The synthesis and detailed characterization of novel hybrid materials with electron acceptor properties has been presented in this work. The hybrid materials were synthesized by functionalizing SWCNTs with semiconducting polymeric quinoline chains using the "grafting from" method. TGA measurements proved the success of the carbon nanotubes functionalization while UV–vis–NIR allowed the band gap estimation for the obtained materials. Raman spectroscopy, in combination with Raman resonance measurements clearly revealed the charge transfer mechanism between the polymer and the SWCNTs suggesting that, due to the preparation pathway, the degree of functionalization of all samples was the same. Furthermore, it was shown that significant electron–photon effects such as Kohn anomalies take place in the metal complex derivative due to the strong coupling between G+ mode with the electron–hole pairs in carbon nanotubes.

The modification in the HOMO position and the electronic structure in the valence band of the materials were revealed by UPS. The attachment of the quinoline molecules in the SWCNTs body lead to a hybrid material with a HOMO position which lays between the HOMO positions of the two starting materials. The herein synthesized hybrid materials are employed for the development of new composites that combine the properties of the corresponding semiconducting polymers with those of the SWCNTs and can be applied in organic solar cells.

AUTHOR INFORMATION

Corresponding Author
*Telephone/Fax: +30 2610 965263/+30 2610 965223. E-mail: siokou@iceth.forth.gr.

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research has been cofinanced by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF), Research Funding Program: Heracleitus II (D.276.001.049). Part of the research leading to these results has received funding from the European Union’s Seventh Framework Programme (FP7/2007–2013) under the Grant Agreement No. 246039. Investing in knowledge society through the European Social Fund. The Technische Universität Berlin authors acknowledge support by the Cluster of Excellence "Unifying Concepts in Catalysis" coordinated by the Technische Universität Berlin and funded by the DFG. J.M. acknowledges support from the European Research Council, ERC Grant No. 259286.

REFERENCES