Chelating Ligands Tethered to Carbon Nanotubes

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Summary: Carbon nanotubes offer an inert platform on which various species may be supported. A range of applications have been addressed using this approach. Anchoring sites on the nanotubes are usually groups introduced *via* an oxidative procedure. These groups provide convenient reactive functionality that can be accessed in a variety of ways. In this case, carboxyl functionality have been utilized to attach, through a linker, a good coordinating ligands, 1-10-phenanthroline. In the first instance, 1,10-phenanthroline was converted to the 5,6-epoxide by treatment with hypochlorite. The epoxide was opened in sulfuric acid to generate the 5-hydroxy compound. This, in turn, was treated with ethylene oxide in the presence of a base to provide the alkoxylated compound. The alcohol terminus, as the alkoxide, was used to couple the nanotubes by displacement of tosyl anion from the methylol ester. The carboxyl groups at the nanotubes surface were reduced to the corresponding alcohol and treated with *p*-toluenesulfonyl chloride in the presence of pyridine to generate the tosylate used for coupling. In a second approach the carboxyl groups were converted to the corresponding acid chloride which was treated with alkoxylated phenanthroline to achieve coupling *via* an ester linkage.

Keywords: chelating ligands; functionalized carbonanotubes; multiwall carbonanotubes; 1,10-phenanthroline

Introduction

Since their discovery nearly two decades ago carbon nanotubes have inspired much work directed toward an understanding of their properties and potential application in a wide range of fields.[1,2–5] Carbon nanotubes are produced commercially by several techniques.[6] These often contain significant levels of impurities, principally metal catalyst residues and amorphous carbon. Impurities may be removed, to a greater or lesser degree, by treatment with acid. Carbon nanotubes are strongly hydrophobic, tend to associate in bundles, and, in an unmodified state, incompatible with many matricies. For most applications the nanotube surface must be modified. While physical methods of surface modification have been widely explored, covalent alteration of the surface has been most useful. Although many methods have been used, this is most generally accomplished by treatment of the nanotubes with a 3:1 mixture of concentrated aqueous sulfuric and nitric acids.[7] This treatment promotes intercalation/exfoliation of the tubes, removes impurities, cuts the tubes (particularly, when acid treatment is used in conjunction with sonication), and effects oxidation at structural defects, principally tube ends, to introduce oxygen-containing functionality, primarily carboxyl groups, at the tube surface. The level of carboxylation achieved has been estimated by a number of methods including acid-base titration,[8,9] infrared spectroscopy,[10] mass increase on salt formation upon reaction with dodecylamine[7] and various microscopy techniques.[4] The presence of carboxyl groups at the surface provides an anchor for the attachment of a variety of groups intended

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to make the nanotubes suitable for a particular application. For the generation of nanocomposites, groups are attached to make the nanotubes compatible with a polymer matrix.[11] In some instances, the polymer may be directly grafted to the nanotube.[12,13] This may be done by either a "grafting to" or "grafting from" approach. The "grafting to" method often utilizes the ability of propagating species to add to the usaturation of the carbon nanotubes.[14–16] In other cases, the preformed end-functionalized polymer is attached by esterification, amidation or other coupling reaction.[17,18] In general, the "grafting to" methods lead to low levels of grafted polymer and non-uniform distribution on the nanotube surface. The "grafting from" approach involves the immobilization of an initiator on the surface of the nanotubes followed by surface-initiated polymerization to grow polymer directly from the nanotube surface.[19] Many kinds of polymers may be attached and high graft density achieved. This approach is amenable to all the quasi-controlled radical polymerization techniques. Attachment of appropriate initiator molecules permits atom transfer radical polymerization (ATRP),[20–23] reversible addition fragmentation chain transfer (RAFT)[24,25] and nitroxyl mediated radical polymerization (NMRP)[26] from the nanotube surface. These methods allow the size of polymer layer at the surface of the nanotube to be controlled.

The utilization of surface-modified carbon nanotubes in biological applications, for example, as biosensors[27] and, more importantly, as drug delivery vehicles[28–33] has great potential. Functionalized, water-soluble carbon nanotubes are able to traverse the cell membrane by endocytosis to deliver a chemotherapeutic agent.[31] This has been wonderfully exploited for the delivery of organoplatinum prodrugs.[32,33] Approximately 65 platinum(IV) units per nanotube may be loaded.[33] This is comparable to the number of (diaminocyclohexane)platinum(II) units that may be attached to the surface of a generation 4.5 poly(amidoamine) [PAMAM] dendrimer.[34] Further, the multi-valent nanotube prodrug may be functionalized with a folate component to specifically target folate receptor-enriched tumor cells.[32]

Experimental Part

Materials

Multi-walled carbon nanotubes COOH functionalized (-COOH content: 2.56 wt%) of 10-50 μm length, 8-15 nm outside diameter and 3-5 nm inside diameter were purchased from Cheap Tubes Inc. All other chemicals were purchased from Aldrich or Alfa Aesar and used as received without further purification. All organic solvents were dried and freshly distilled prior to use.

Methods and Instrumentation

Thermogravimetric analyses (TGA) were carried out using a TA Instruments model 2950 TGA unit interfaced with the 2100 control module. The TGA cell was swept with nitrogen or air at 20 mL/min during degradation runs. The sample size was 5-10 mg in a platinum sample pan. Heating rate: 10 °C min^{-1}, after equilibration at 40 °C. Fourier transform infrared (FT-IR) spectra were obtained using solid solutions (~1%) in anhydrous potassium bromide (as pellets) using a model 560 Nicolet MAGN-IR spectrophotometer. Nuclear magnetic resonance (NMR) spectra (^1H and ^{13}C) were obtained using solutions in DMSO-d_6 or $CDCl_3$ containing tetramethylsilane (TMS) as an internal reference and a Varian Plus 300 spectrometer. Direct insertion probe mass spectrometry (DIP-MS) was used to determine the molecular weights of the phenanthroline compounds. Bath sonication (Branson 3510) and filtration using polycarbonate membrane filters (Millipore) were employed for the reactions/separations of functionalized MWNTs.

Synthesis

1,10-Phenanthroline-5,6-epoxide

As previously reported,[35–39] 1,10-phenanthroline-5,6-epoxide was obtained by hypochlorite oxidation of 1,10-phenanthroline in

93.2% yield as a yellow powder, m.p. 160-162 °C: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.6 ppm (2H, s, phenH-5&6), 7.36-7.4 ppm (2H, dd 7.6, 4.6 Hz, phenH-8 + 3), 7.97-8.0 ppm (2H, dd 7.6, 1.7 Hz, phenH-4 + 7), 8.89-8.91 ppm (2H, dd, 4.6, 1.7, phenH9&2); ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ 150.39 ($C_2 + C_9$), 149.03 ($C_{10a} + C_{10b}$), 137.95 ($C_4 + C_7$), 128.78 ($C_{4a} + C_{6a}$), 123.423 ($C_8 + C_3$), 54.83 ($C_5 + C_6$); IR (KBr): 3003, 1579, 1560, 1475, 1431, 1216, 1189, 1131, 1080, 1012, 883, 799, 750, 705 cm^{-1}.

5-Hydroxy-1,10-phenanthroline Monohydrate

Using modification of a previously reported procedure,[38,40,41] 5-hydroxy- 1,10-phenanthroline monohydrate was obtained in 88.75% yield as a dark red solid, m.p. 210-211 °C: ^{1}H-NMR (300 MHz, DMSO-d_6) δ 10.9 (broad, s, 1H, OH), 9.09 (1H, d, phenH-2), 8.8 (1H, d J 8.2 Hz, phenH-9), 8.6 (1H, d J 7.8, phenH-4), 8.23 (1H, d, J 8.2 Hz, phenH-7), 7.72-7.76 (1H, dd J 8.2, 4.3 Hz, phenH-3), 7.57-7.61 (1H, dd J 8.2, 4.3 Hz, phenH-8), 7.12 (1H, s, phen H-6), 3.4 (s, H_2O); ^{13}C-NMR (75.46 MHz, CD_3OD) δ 150.85 (C_5), 150.07 (C_2), 146.6 (C_{10a}), 146.4 (C_9), 1461.53(C_{10b}), 134.14 (C_4), 130.51 (C_7), 129.65 (C_{6a}), 123.31 (C_3), 123.19 (C_8), 122.77 (C_{4a}), 103.93 (C_6); IR (KBr): 3438, 2955, 1652, 1506, 1419, 1124, 1070, 1008, 832, 739, 703 cm^{-1}; DIP-MS: calcd. for $C_{12}H_8N_2O$ 196, found 196. The solid is insoluble in usual organic solvents such as: chloroform, methylene chloride, acetone, ethyl acetate, toluene, acetonitrile, DMF, THF, ether but is slightly soluble in DMSO and methanol.

5-(2-Hydroxyethoxy)-1,10-phenanthroline

A solution of 5-hydroxy-1,10-phenanthroline monohydrate (428 mg, 2.00 mmol) and potassium carbonate (304 mg, 2.2 mmol) in 10 mL of DMF was stirred at 60 °C under nitrogen for two hours. A clear orange solution was formed and allowed to cool to room temperature. Ethylene oxide was bubbled into the stirred solution for 20 minutes (at a rate of about 1 bubble per second). A slight exothermic effect was noticed and the color of the solution changed to maroon. The mixture was then stirred at room temperature for three hours and a new portion of ethylene oxide was bubbled into the solution for 10 minutes (no changes in the appearance of the solution were noticed). The mixture was stirred overnight at room temperature, neutralized to pH = 7 with concentrated aqueous sulfuric acid solution, and the solvent distilled at reduced pressure. A dark red powder was obtained: ^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.95 (dd, J = 1.5, 4.2 Hz, 1H), 8.72-8.80 (m, 1H); 8.51 (m, 1H), 7.78-7.88 (m, 1H), 7.58-7.68 (m, 1H), 7.34 (dd, J = 4.2; 8.1, 1H), 6.72 (s, 1H), 4.28 (t, J = 4.4, 2H), 3.91 (t, J = 4.4, 2H); IR (KBr): 3406, 2935, 2627, 1653, 1506, 1419, 1301, 1259, 1218, 1124, 1071, 1008, 981, 831, 739, 703 cm^{-1}. The product is insoluble in almost all organic solvents and has a very modest solubility in DMSO and methanol. The DIP-MS spectrum contained a molecular ion peak at m/z 240, consistent with the attachement of a single ethylene oxide residue to the phenolic hydroxy group.[38,42]

MWCNT-CH_2OH

To a stirred solution of 3.65 g MWCNT (2.56% carboxy-functionalized; 0.093 g, 2.07 mmole of carboxyl functionality) in 100 mL of anhydrous THF was added, dropwise, over a period of 0.25 hr, a solution of 1M borane in THF (3.5 mL, 3.5 mmol). Upon completion of the addition, the mixture was allowed to stir overnight ar room temperature. Water (10 mL) was added to remove excess borane and the suspended solid collected by filtration at reduced pressure. The solid was washed repetedly with acetone and then dried at reduced pressure to provide MWCNT-CH_2OH.[43,44]

MWCNT- CH_2OTs

To a stirred suspension of 3.50 g MWNT-CH_2OH and 1 mL (0.726 g, 7.18 mmole) of triethylamine in 100 mL of dry dichloromethane maintained in a nitrogen atmosphere was added, dropwise, over a period of 0.25 hr., a solution of 0.43 g (2 mmol) of

p-toluenesulfonyl chloride in 10 mL dichloromethane. The resulting mixture was stirred 16 hours at room temperature. The nanotubes were collected by filtration at reduced pressure and washed, succesively, with several portions of first dichloromethane and then methanol.[45,46]

MWCNT-Phen-ether

To a stirred solution of 5-(2-hydroxyethoxy)-1,10-phenanthroline (200 mg, 0.833 mmol) in 10 mL DMF maintained in a nitrogen atmosphere was added 36 mg (0.9 mmol; 60% suspension in mineral oil) of sodium hydride. Hydrogen evolution was noted. The solution was stirred for 0.5 hr at room temperature. A suspension of 1.58 g MWCNT-CH_2OTs (0.9 mmol of tosylate functionality) was added and the resulting mixture was stirred 24 hr at room temperature. The solid was collected by filtration at reduced pressure, washed with several portions of methanol and acetone, and dried at reduced pressure and room temperature.

MWCNT-COCl

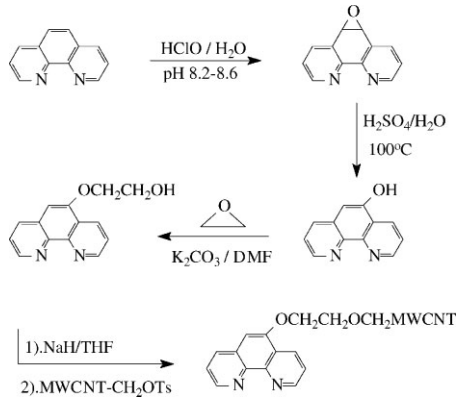
A suspension of 500 mg MWCNT-COOH (2.56% carboxy-functionalized; 12.8 mg, 0.28 mmole of carboxyl functionality) in 250 mL thionyl chloride containing a few drops of *N*,*N*-dimethyldimethylformamide (DMF) was subjected to sonication for 0.5 hr and then stirred at thionyl chloride reflux for 24 hr. The MWCNT-COCl was collected by filtration at reduced pressure, washed with several portions of THF and dried at reduced pressure and room temperature.

MWCNT-Phen-ester

To a cold (0 °C), stirred suspension of 200 mg MWCNT-COCl (7.22 mg, 0.11 mmole of acid chloride functionality) in 150 mL of DMF was added, portionwise, a solution of 200 mg (0.83 mmol) of 5-(2-hydroxyethoxy)-1,10-phenanthroline and 5.0 mL (4.9 g, 0.061 mole) of pyridine in 25 mL of DMF. The resulting mixture was maintained in a nitrogen atmosphere with constant stirring and intermitant sonication for three days. The solid was collected by filtration at reduced pressure, washed with several portions of methanol, and dried at reduced pressure and room temperature.

Results and Discussion

1,10-Phenanthroline presents several attractive structural and chemical properties. Perhaps, the greatest of these is its remarkable chelating capability.[47,48] 1,10-Phenanthroline forms stable complexes with a wide variety of metal cations including, importantly, those of the platinum group metals.[35,49] Attachment of a phenanthroline moiety to a stable, relatively inert platform could form the base for a family of heterogeneous catalysts that would be readily separable from product mixtures and recyclable. In this instance, 1,10-phenanthroline has been anchored to multi-walled carbon nanotubes (MWCNT) *via* a tether. The most suitable route to an appropriate structure is shown in Scheme 1. 1,10-Phenanthroline was converted to the 5,6-epoxide by treatment of a dichloromethane solution with aqueous hypochlorite in the presence of a phase-transfer catalyst at pH 8.4.[35–39] The pH of the aqueous phase must be maintained between 8.2-8.6. At higher pH very little epoxidation occurs and at lower pH other oxidation products, principally 5,6-dichloro-5,6-dihydro-1,10-phenanthroline



Scheme 1.
Attachment of a 1,10- phenanthroline unit to MWCNT *via* an ethylenedioxy tether.

and 5-chloro-6-hydroxy-5,6-dihydro-1,10-phenanthroline, are formed.

Conversion of the epoxide to 5-hydroxy-1,10-phenanthroline could be accomplished by treating it with concentrated aqueous sulfuric acid.[38,40,41] This transformation is reflected in the proton NMR spectra contained in Figure 1. The spectrum for the 5-hydroxy compound contains absorption at δ 7.12 for the proton at C-6 and at δ 10.9 for the hydroxyl proton. 5-Hydroxy-1,10-phenanthroline is insoluble in most organic solvents but is modestly soluble in dimethyl sulfoxide and methanol. It displays an onset temperature for degradation of 329 °C as determined by thermogravimetry.

5-Hydroxy-1,10-phenanthroline was converted to the corresponding 2-hydroxyethyl ether by treatment with ethylene oxide in dimethylformamide in the presence of potassium carbonate.[38,42] Conversion of the alcohol to the alkoxide and treatment with MWCNT containing primary tosylate groups at the surface permitted coupling to the nanotubes. The tosylate functionalized tubes were prepared by borane reduction of carboxy functionalized tubes followed by esterification with *p*-toluenesulfonyl chloride (Scheme 2).[43–46]

These transformations were most conveniently monitored by thermogravimetry and infrared spectroscopy. Figure 2 contains decomposition thermograms for

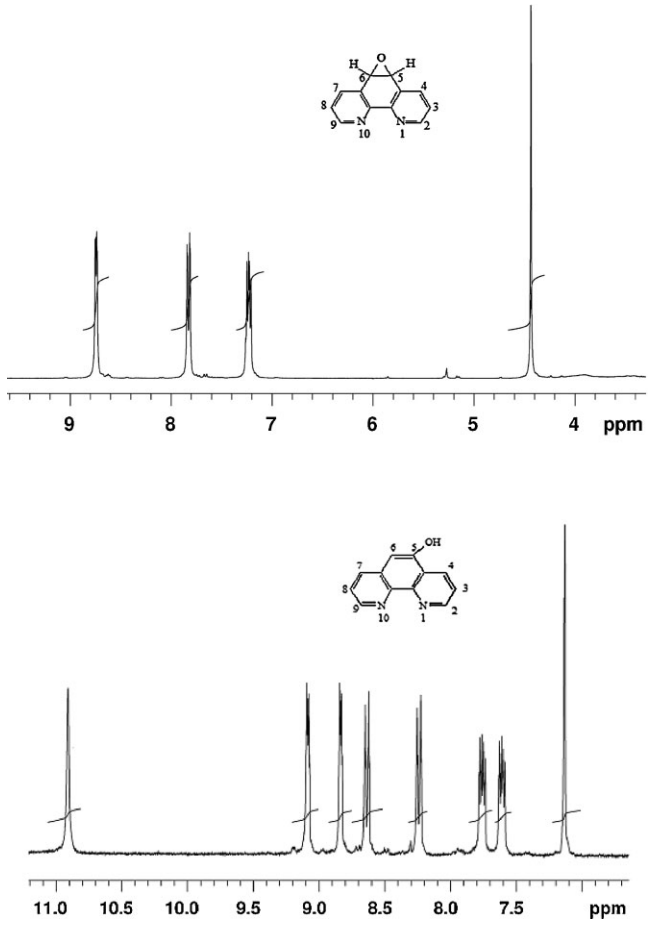
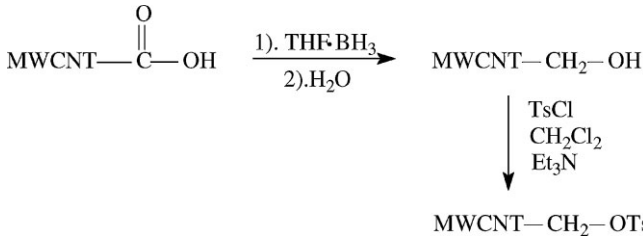


Figure 1.
Proton NMR spectra of 1,10-phenanthroline-5,6-epoxide and 5-hydroxy-1,10-phenanthroline.



Scheme 2.
Generation of tosylate functionalized MWCNT.

functionalized nanotubes, carboxyl through the ether-linked phenanthroline ligand. The indicated transformations are clearly evident in these thermograms.

Consistent with earlier observations, nanotubes with more complex substitution display lower thermal stability than do the corresponding structures with simplier substituents.[21,22,26] It has been suggested that the presence of substituent fragments and a less perfect structure after modification make carbon nanotubes more suspectable to thermal degradation.[21] This is reflected in the plots contained in Figure 2. The sample of MWCNT-COOH decomposes slowly ($T_{onset} \sim 813\,^{\circ}C$; weight loss at $600\,^{\circ}C$ ~10%) with the increasing of temperature most likely because of the loss of carboxyl groups at the surface of the MWCNT. Upon functionalization, the nanotubes degrade at significantly lower temperatures, e.g., T_{onset} for MWCNT-CH_2OH ~$455\,^{\circ}C$ and a mass loss of ~80%); T_{onset} for MWCNT-CH_2OTs ~$499\,^{\circ}C$ with a mass loss of ~79%; T_{onset} for MWCNT-Phen-ether ~$398\,^{\circ}C$ with a mass loss of ~68%.

The thermogram for decomposition of the ether-linked phenanthroline derivative is displayed in Figure 3. This derivative undergoes decomposition with an extrapolated onset temperature of ~$398\,^{\circ}C$ to yield a residue of 32% of the initial sample mass at $600\,^{\circ}C$.

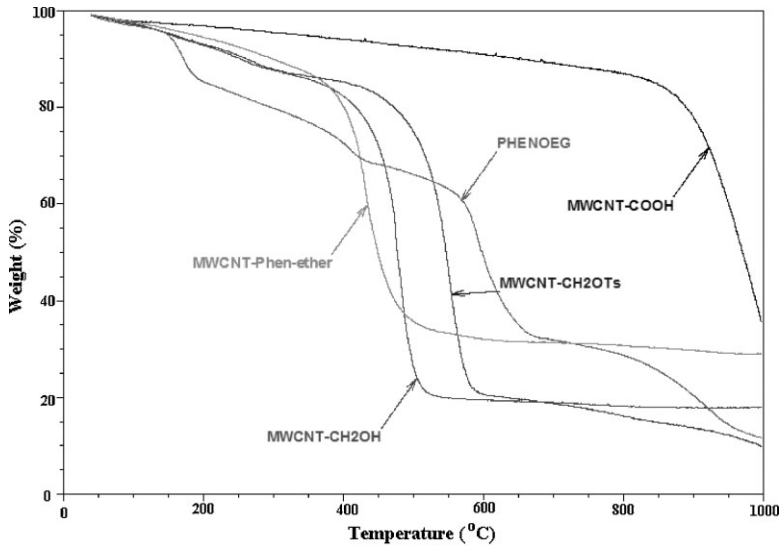


Figure 2.
Thermal degradation in a nitrogen atmosphere of functionalized MWCNT-carboxyl through ether-linked phenanthroline.

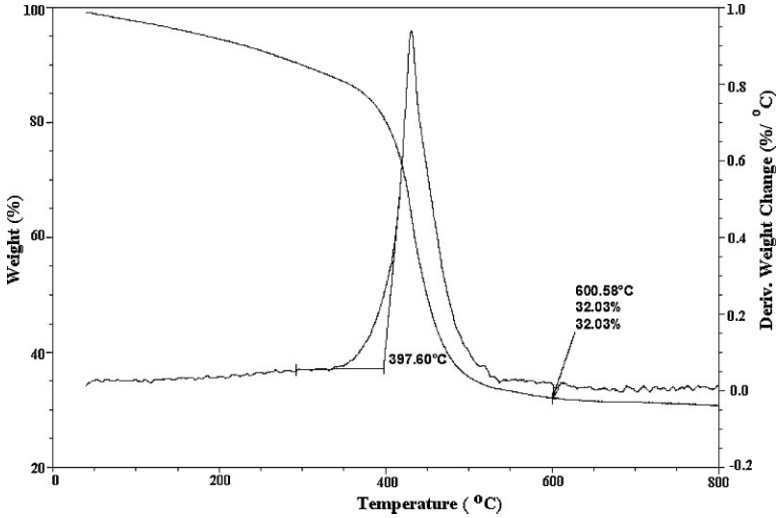


Figure 3.
Thermal degradation in a nitrogen atmosphere of MWCNT containing ether-linked phenanthroline at the surface.

The infrared spectra of the various adducts are also supportive of the structures indicated (see Figure 4).

As noted on the spectra, expected changes occur as the carboxyl-functionalized MWCNT are converted to the corresponding phenanthroline-functionalized material. In the FTIR spectrum of oxidized MWCNT (A), the peak at $\sim 1720\,cm^{-1}$ may be attributed to the C=O stretch of the carboxylic (COOH) group and the peak at about $3400\,cm^{-1}$, to the hydroxyl band. The infrared spectrum of the material treated with borane complex (trace B) shows the reduction of the carboxyl groups from MWCNT-COOH to hydroxymethyl

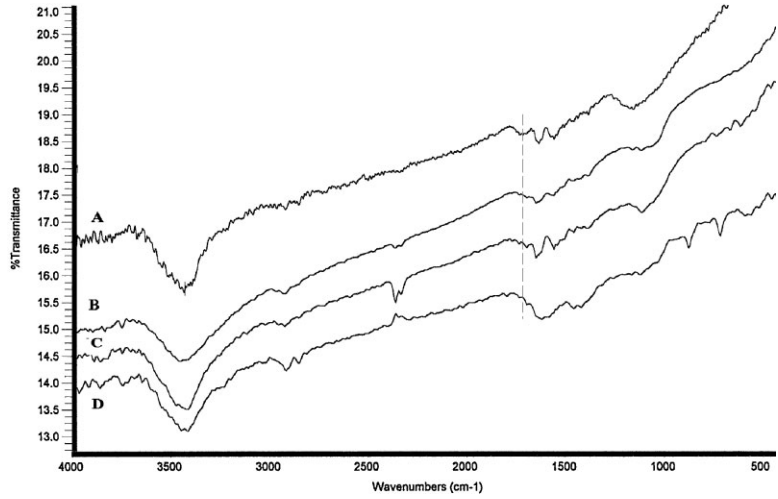
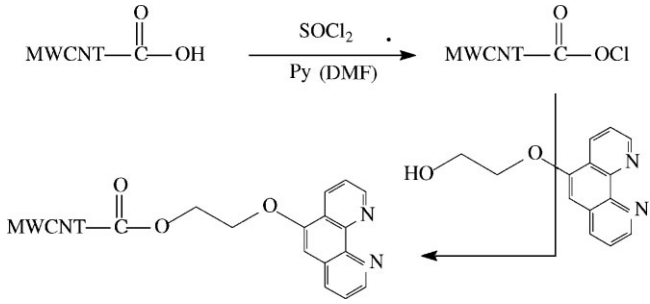


Figure 4.
Infrared spectra of functionalized MWCNT-carboxyl through ether-linked phenanthroline. MWCNT-COOH (A), MWCNT-CH2OH (B), MWCNT-CH2OTs (C), MWCNT-Phen-ether (D).



Scheme 3.
Attachement of a 1,10-phenanthroline unit to MWCNT *via* an ester linkage.

(MWCNT-CH2OH) as indicated by the disappearance of the C=O bands and the appearance of two small peaks at ~2900 and 2850 cm^{-1} corresponding to the C–H stretching vibrations of the methylene group. The infrared spectrum for MWCNT-CH2OTs contains bands characteristic of tosylate esters at approximately 1190, 1380 and 660 cm^{-1}. The FTIR spectrum of the MWCNT-Phen-ether presents several characteristic bands: C-O-C stretch at about 1120 and 1300 cm^{-1}; aromatic nucleus at ~1600 and 1475; C-N stretch (aryl) at 1360 cm^{-1}. Also C-H (aromatic) bands are present at about 690 and 880 cm^{-1} (bend) and 3020 cm^{-1} (stretch).

In a second approach (Scheme 3), carboxyl groups at the surface of the nanotubes were converted to the corresponding acid chloride and treated with 5-(2-hydroxyethoxy)-1,10-phenanthroline to attach the phenanthroline ligand *via* an ester linkage. This adduct was also characterized using thermogravimetry and infrared spectroscopy. Thermograms for the decomposition of the carboxy-functionalized MWCNT, the corresponding acid chloride and the ester-bound 1,10-phenanthroline are displayed in Figure 5.

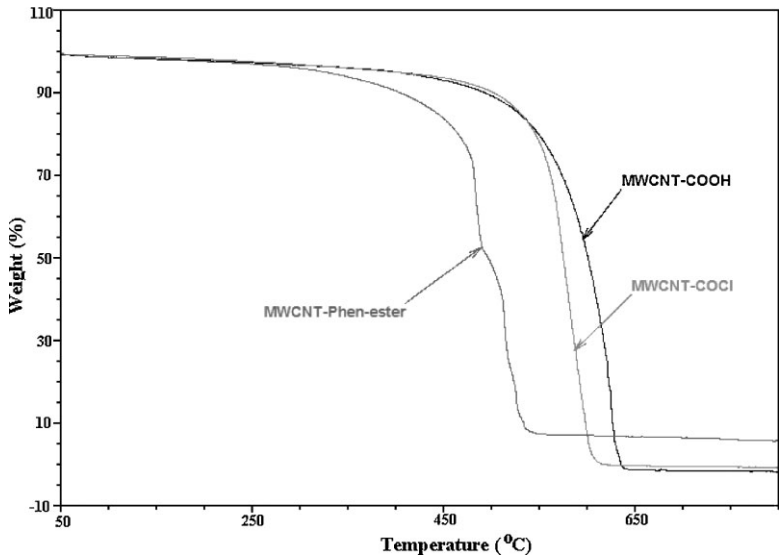


Figure 5.
Thermal degradation in an air atmosphere of functionalized MWCNT-carboxyl through ester-linked phenanthroline.

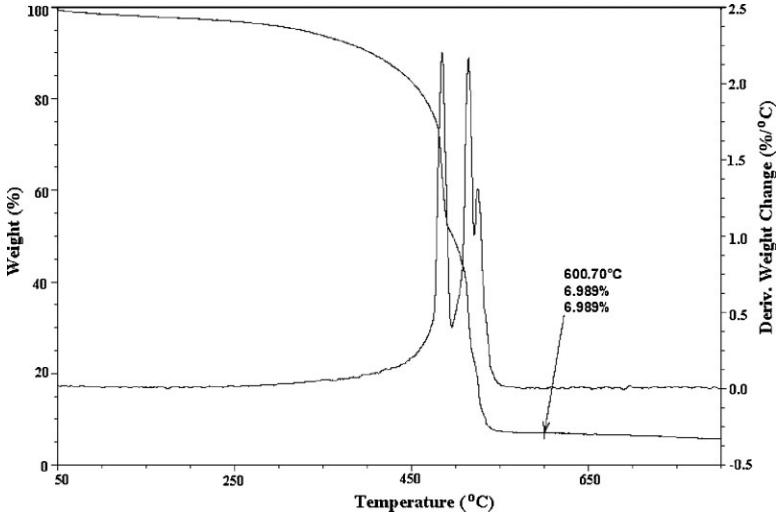


Figure 6.
Thermal degradation in an air atmosphere of MWCNT containing ester-linked phenanthroline at the surface.

The thermogram for the decomposition (in air) of the ester precursor is included for comparison. The thermal degradation of the ester-bound-1,10-phenanthroline-MWCNT is depicted in Figure 6.

The thermograms for MWCNT-COOH and MWCNT-COCl show that the onset temperature with apparent weight loss occurs above 600 °C (640 °C for MWCNT-COOH and 617 °C for MWCNT-COCl, respectively). Decomposition of the sample having the phenanthroline fragment attached occurs smoothly in three stages with extrapolated degradation onset temperatures of 477 °C, 509 °C, and 524 °C, respectively and reflects fragmentation of the attached ligand.

The infrared spectra of the carboxy-functionalized MWCNT, the corresponding acid chloride, and the ester-linked

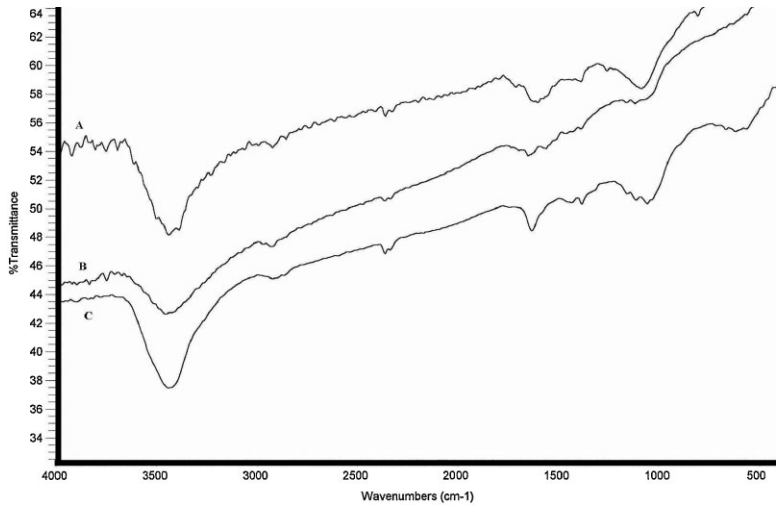


Figure 7.
Infrared spectra of carboxy-functionalized MWCNT (MWCNT-COOH, A), the corresponding acid chloride (MWCNT-COCl, B), and ester-linked phenanthroline-MWCNT (MWCNT-Phen-ester, C).

phenanthroline-MWCNT adduct are presented in Figure 7.

In the ester-linked phenanthroline - MWCNT (MWCNT-Phen-ester) the most interesting band is that found at about 1735 cm^{-1} (as compared to 1720 cm^{-1} in MWNT-COOH (A) and 1710 cm^{-1} in MWNT-COCl (B) indicating that phenanthroline ligand was covalently bound to the MWCNT through an ester linkage.

Conclusion

1,10-Phenanthroline, a good metal-complexing ligand, has been linked to MWCNT by both ether and ester linkages. The ether-linked adduct might be expected to be stable to a wider range of potential reactions conditions than would be the ester-linked adduct. However, either should be suitable for many applications. In particular, these adducts should form the base for robust heterogeneous catalyst systems that may be recycled repeatedly.

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