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Repetitive Functionalization of Water-Soluble Single-Walled Carbon Nanotubes. Addition of Acid-Sensitive Addends

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A method has been developed for creating bulk quantities of water-soluble single-walled carbon nanotubes (SWNTs) that contain multifunctional, acid-sensitive addends. Utilizing aryl diazonium salts, the repetitive functionalization protocol can yield multifunctional SWNTs containing moieties that would not be stable to the harsh oleum functionalization conditions used previously. The presence of multifunctionality on the SWNTs has been confirmed using Raman spectroscopy, thermal gravimetric analysis, and X-ray photoelectron spectroscopy.

Introduction

The preparation of water-soluble single-walled carbon nanotubes (SWNTs) in bulk quantities has been addressed in the literature.[1−8] This paper describes an expansion on the technique which leads to highly customized, individually suspended aqueous SWNT systems. The protocol does not require high-powered sonication or centrifugation, which are limitations of previous methods to generate individual SWNTs. The previously reported bulk preparation method for producing water-soluble SWNTs relies upon using oleum (fuming sulfuric acid; H_2SO_4 with dissolved SO_3) to disperse the SWNTs as individuals followed by functionalization via diazonium chemistry. Here, we take those newly generated water-soluble SWNTs and functionalize them further in water only as a solvent, thereby permitting the second functionalization addends to be chemically sensitive[9] functional groups that are not able to withstand strongly acidic conditions. This allows for the synthesis of SWNTs containing functional groups that are not accessible via the oleum method alone, such as biologically important molecules that would decompose under the oleum conditions.[10] By using the oleum procedure as the source for individualized SWNTs, and following up with aqueous aryldiazonium chemistry, it is possible to obtain water-soluble SWNTs with a variety of functional groups that can be customized to fit a desired application.

A potential application of multifunctional SWNTs would be as drug delivery agents. One way to overcome the adverse effects of some drug treatments is to mask the drug, or make it inactive, until it reaches the location of action. Once the masked drug has reached its destination, it can then be unmasked to reveal the active compound only in the targeted disease area. Masked drugs are commonly known as prodrugs and have been used extensively in medicine to treat a number of conditions.[11] A further extension of this concept is to use a multifunctional nanosized particle that has a combination of features including the ability to transport drugs, to target specific cells or areas of the body, the ability to traverse specific membranes and barriers, and to fluoresce or act as a contrast agent, while remaining soluble in a biological system.[12] A multifunctional SWNT could contain some or all of these features.

Repetitive Functionalization

To produce water-soluble SWNTs, we used the oleum method[1] to add sulfonated 4-chlorophenyl moieties to the sidewalls of the SWNTs to give **1**. Scheme 1 shows the general method for functionalizing SWNTs in a repetitive functionalization method. After initial functionalization, **1** was dispersed in water by homogenization and treated with a variety of diazonium salts. The diazonium salts functionalized the tubes and provided a bimodal functionality to the sidewall of the SWNTs. Some arene radical addition to the existing pendants will occur with the addition of the

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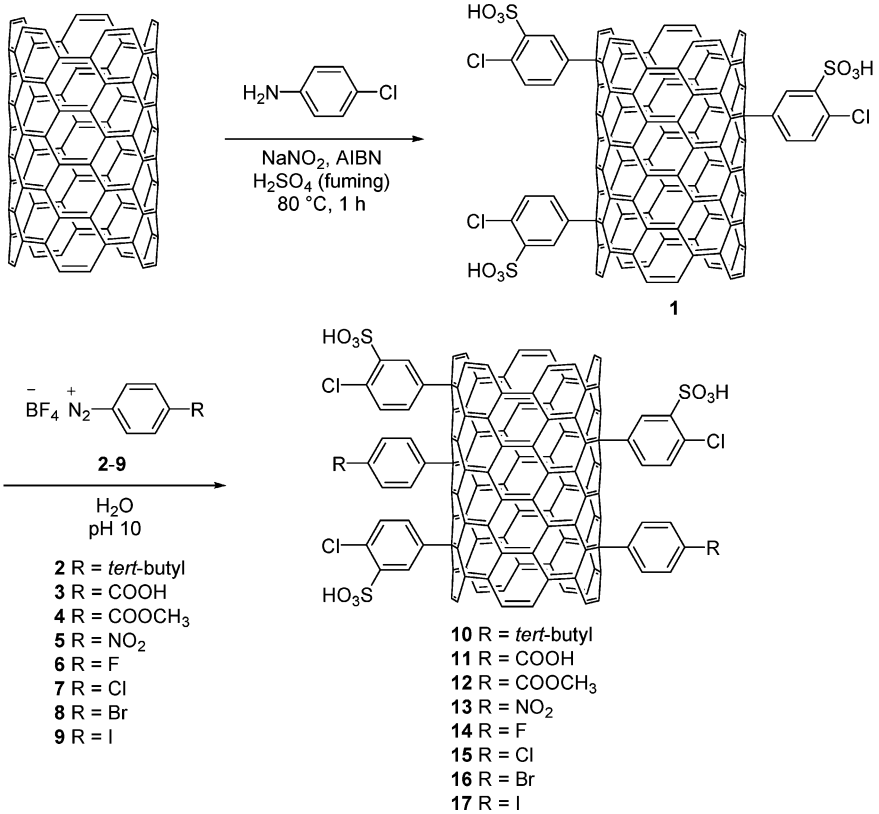
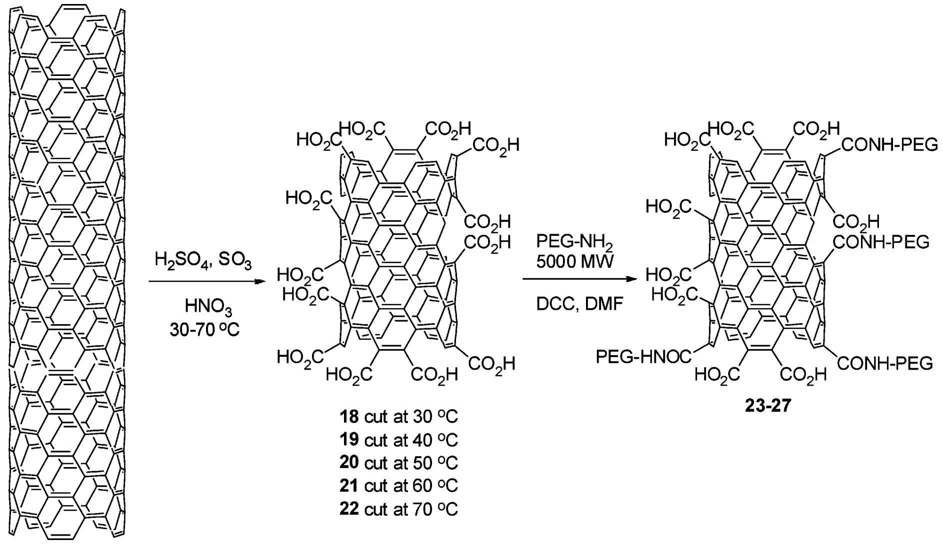
Scheme 1. Repetitive Functionalization Protocol[a]



[a] Water-soluble SWNTs (**1**) are reacted with a variety of diazonium salts (**2**−**9**) to produce multifunctional SWNTs **10**−**17**.

Scheme 2. US-SWNTs 18−22 That Are Produced by Chemically Cutting and Oxidizing SWNTs at Varying Reaction Temperatures Are Coupled with PEG-amine to Make PEGylated US-SWNTs 23−27, Respectively



diazonium salt, but Raman analyses confirm further sidewall attachment.

The second technique for providing water-soluble SWNTs was to make carboxylated ultrashort-SWNTs (US-SWNTs) by cutting the nanotubes in a mixture of oleum and nitric acid;[13] shorter lengths of cut SWNTs can be obtained by increasing the cutting temperature (from 30 °C yielding 98 nm average length to 70 °C yielding 32 nm average length).[13,14] These tubes contain defect sites with carboxylic acids that can be exploited for further functionalization. The US-SWNTs were then treated with poly(ethylene glycol) (PEG)-amine and *N*,*N*-dicyclohexylcarbodiimide (DCC) in dry DMF to covalently bind the PEG chains to some of the carboxylic acids located at the defect sites (Scheme 2).[15,16]

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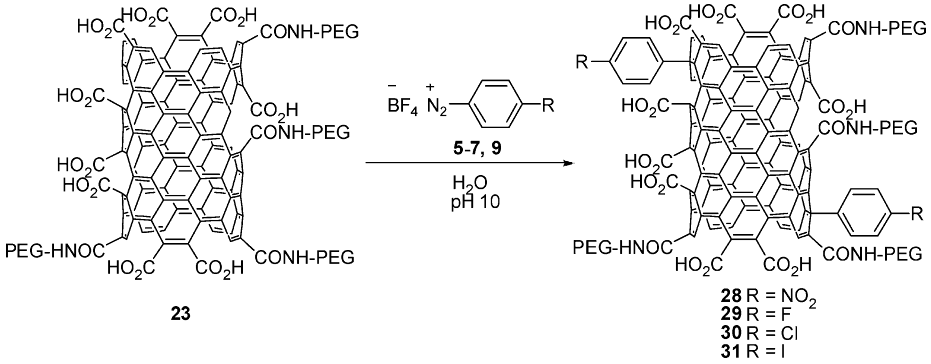
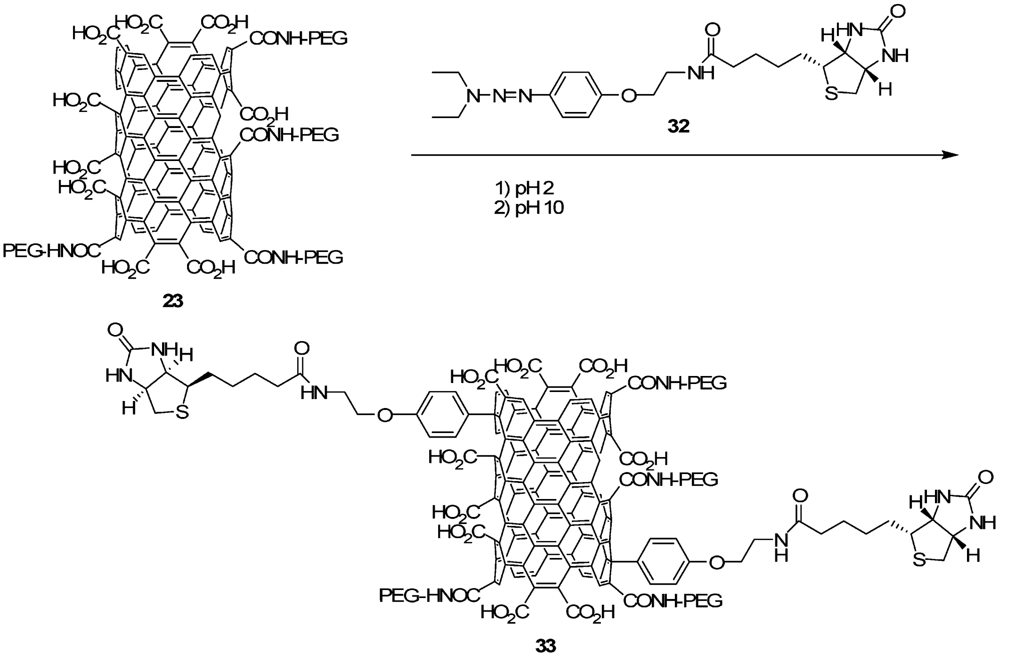
Scheme 3. Water-Soluble PEGylated US-SWNTs (23) Are Functionalized with a Variety of Diazonium Salts (5−7, 9) To Produce PEGylated US-SWNTs 28−31, Respectively, That Are Multifunctional



Scheme 4. Water-Soluble PEGylated US-SWNTs (23) Are Functionalized with an Acid-Sensitive Moiety, Biotin, To Produce a Water-Soluble Multifunctional SWNT (33)



After this process was complete, the material was transferred to a dialysis bag (50000 MWCO) and dialyzed with water for 5 d to remove any unbound PEG-amine. This process yielded material that is soluble in water, irrigation saline, and phosphate buffered saline (PBS). To test solubility in PBS and irrigation saline, the concentrated PEGylated US-SWNTs, in water, were diluted with PBS or saline. A typical dilution consisted of 1 part PEGylated US-SWNTs to 1 part PBS or irrigation saline.

Table 1. Raman D/G Ratio and TGA-Determined Weight Loss for Functionalized SWNTs 1, 10−17[a]

compd	Raman D/G	TGA wt loss (%)	functional group coverage
1	0.38	29	1/30
10	0.55	35	1/20
11	0.58	31	1/20
12	0.76	40	1/25
13	0.65	36	1/21
14	0.65	23	1/27
15	0.58	34	1/18
16	0.62	43	1/17
17	0.63	53	1/15

[a] Representative Raman (633 nm excitation) D/G values averaged over five scans per sample. TGA results show total mass loss. Total mass loss was attributed to functional groups covalently attached to the sidewall. With use of the mass loss and the molecular weight of the functional group fragment, the number of moles of functional groups present was calculated. With the moles of both functional groups present and SWNT carbons, the functional group to SWNT carbon ratio was calculated.

The water-soluble PEGylated US-SWNTs that were cut at room temperature (**23**) then underwent diazonium salt functionalization using a variety of diazonium salts (**5**−**7**, **9**) as shown in Scheme 3. This again gives multifunctionality to the SWNTs **28**−**31**. These PEGylated US-SWNTs remained soluble in water after the repetitive functionalization.

Table 2. XPS Data for Compounds 1 and 10−17

compd	C (%)	O (%)	N (%)	Br (%)	S (%)	I (%)	F (%)	Cl (%)
1	76.6	15.8	2.9		2.69			2.27
10	86.1	9.1	1.7		1.6			1.4
11	72.0	20.1	2.3		3.7			1.8
12	77.3	18.2	1.3		1.6			1.5
13	76.4	15.0	5.5		1.6			1.5
14	67.6	24.2	4.0		1.2		3.1	
15	80.6	10.5	1.7		1.3		0	6.0
16	82.1	10.7	0.9	3.6	1.2		0.03	1.3
17	78.5	10.8	5.1		0.8	4.12	0	0.7

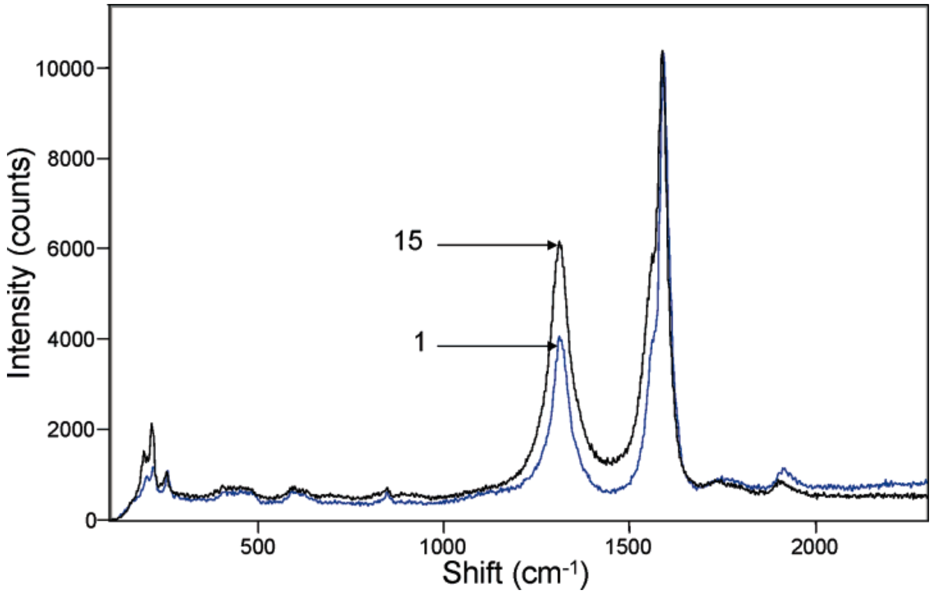


Figure 1. Representative Raman spectrum (633 nm excitation) showing starting material **1** and repetitive functionalization product **15**. The increase of the D band in **15** is indicative of an increase in sidewall functionalization.

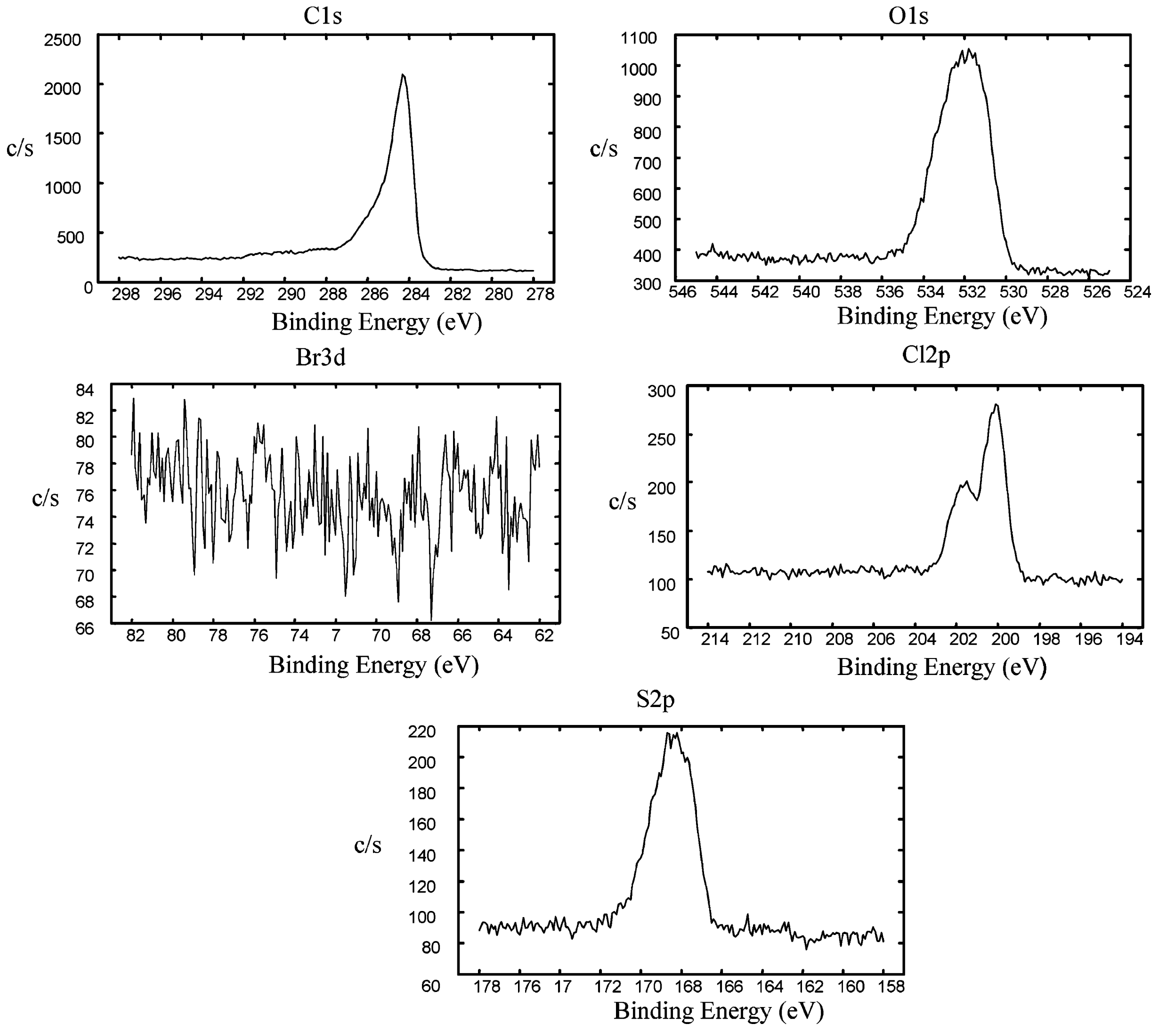


Figure 2. XPS analysis of SWNT **1** bearing chloroarylsulfonic acid addends; no bromine was detected.

The PEGylated US-SWNTs were then functionalized with acid-sensitive moieties. For example, biotin was attached to the SWNTs, while still maintaining water and PBS solubility as shown in Scheme 4.

Characterization

Each of the SWNT products from repetitive functionalizations (**10**−**17**) showed an increase in the D/G ratio in the

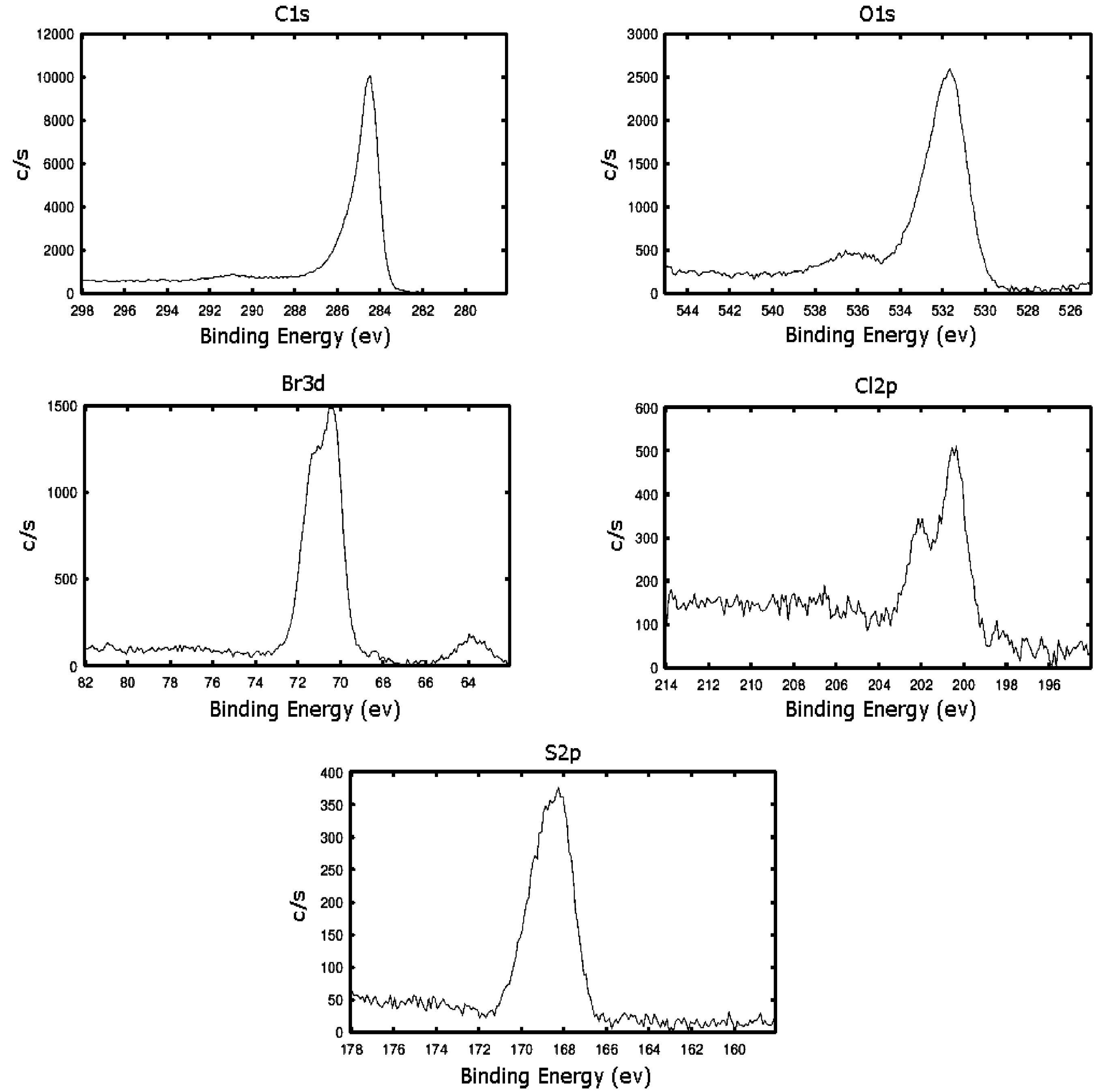


Figure 3. XPS analysis of SWNT **16** bearing aryl bromide addends. The XPS result indicates the presence of both chloride and bromide addends.

Raman spectrum compared to arylsulfonic acid SWNT **1**. The D/G ratio is the ratio of the disorder mode (diamondoid or D-band, 1290 cm^{-1}), characteristic of the sp^3-hybridized carbons, compared to the tangential mode (graphitic or G-band, 1594 cm^{-1}), characteristic of the sp^2-hybridized carbons remaining on the nanotube.[9a] Figure 1 is a representative Raman spectrum showing an increase in the functionalization of **15** compared to **1** by the increase of the D band. Table 1 shows the Raman D/G value for each functionalized product and a calculation for the functional groups per nanotube carbon based on thermogravimetric analysis (TGA) weight loss.

X-ray photoelectron spectroscopy (XPS) analysis (Table 2) was used in conjunction with Raman and TGA to confirm the presence of added functional groups to the sidewall of **1**.

TGA weight loss was not significant in some cases (**11**, **14**) compared to the starting material (**1**), but the Raman and XPS data strongly support the conclusion that functionalization did occur. Increased functionalization of these SWNT products was noted due to increased halogen (**14**−**17**) and nitro (**13**) signals in the XPS analysis. The hydrocarbon and carboxy SWNTs (**10**−**12**) are more difficult to distinguish by XPS due to the inability to distinguish between the SWNT carbon and the addend carbon. Figure 2 shows an XPS analysis of **1** with aryl chloride functionalization. There was no bromine detected whereas Figure 3 shows an XPS analysis of **16**, revealing the bromine from

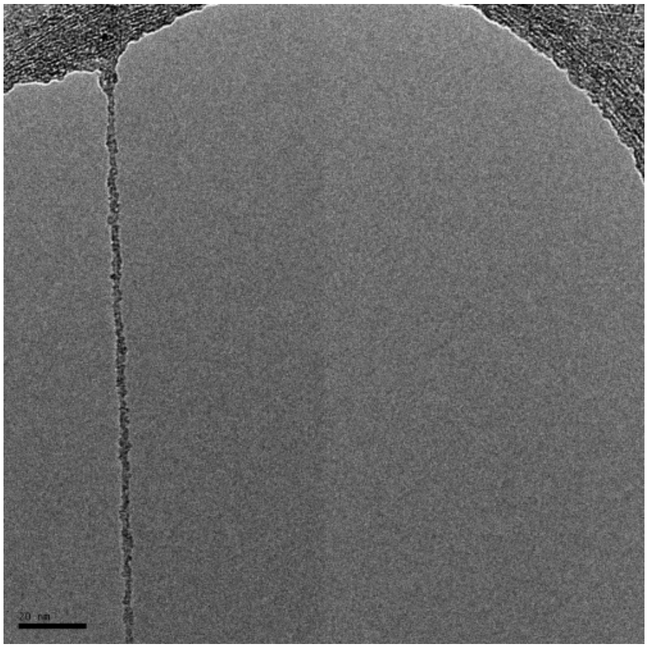


Figure 4. TEM of **11** deposited from a solution in water onto a holey lacey carbon grid. This image shows an individual SWNT functionalized first with arylchlorosulfonic acid followed by functionalization with benzoic acid diazonium salt. The bumps on the sidewall are from the aryl functionalities on the SWNT. The scale bar is 20 nm.

Table 3. Raman D/G Ratio and XPS Analysis of Products 23 and 28−31

compd	Raman D/G	C (%)	O (%)	N (%)	Br (%)	S (%)	I (%)	F (%)	Cl (%)
23	0.44	65.9	30.3	3.4	0.2	0.2	0.0	0.0	0.0
28	0.53	67.7	24.8	7.0	0.0	0.2	0.0	0.2	0.0
29	0.62	72.2	17.4	6.3	0.0	0.1	0.0	4.0	0.0
30	0.75	71.9	19.4	4.1	0.0	0.4	0.0	0.0	4.1
31	0.82	61.4	28.1	8.4	0.2	0.1	0.7	0.0	1.1

the addend attached through the repetitive functionalization method.

Transmission electron microscopy (TEM) indicated that the SWNTs were individuals after functionalization of **1** using aryldiazonium salts (**2**−**9**) in water. A representative TEM of **11** (Figure 4) indicates the presence of individual SWNTs with a roughened sidewall surface, which has been attributed to the aryl moieties attached to the tube wall.[10]

Repetitive Functionalization of PEGylated US-SWNTs

The PEGylated US-SWNTs that underwent repetitive functionalization (**28**−**31**) showed an increase in D/G ratio compared to the starting PEGylated US-SWNTs (**23**) as indicated in Table 3. This increase confirms that functionalization occurred. Table 3 also contains the XPS data which shows an increase in the corresponding halogen content for diazonium salt functionalization in comparison to the PEGylated US-SWNTs (**23**). The nitrogen present in the sample is attributed to the presence of aryldiazo moieties and N_2 surface contamination.

The TGA data implies that continued functionalization of the PEGylated shortened SWNTs stabilizes the PEGylated shortened SWNTs, causing the weight loss to decrease in comparison to the unfunctionalized shortened SWNTs (**23**).

Conclusion

A method for the bulk preparation of water-soluble SWNTs which does not use high-powered sonication or centrifugation has been developed. This allows for repetitive functionalization with aryl groups that would not be stable to functionalization using oleum as the solvent. We have also shown that water and PBS-soluble US-SWNTs can be made by first cutting the SWNTs with oleum and nitric acid followed by PEGylation. These PEGylated US-SWNTs then undergo repetitive functionalization in water using diazonium salt chemistry to produce multifunctional water and PBS-soluble US-SWNTs.

Experimental Section

General Methods. Amine-terminated poly(ethylene glycol) was obtained from Nektar (5000 MW, Catalog #: 2M2U0H01, Lot #: PT-02F-13). Purified SWNTs[17] were obtained from Rice University HiPco laboratory. All other starting compounds were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. Thermogravimetric analysis was performed from room temperature to 850 °C at 10 °C/min under argon. Raman spectroscopy was performed on a Renishaw Raman scope using a 633 nm He−Ne laser, taking the median of five scans. XPS was carried out on a PHI Quantera SXM Scanning X-ray Microprobe with a pass energy of 26.00 eV, 45° takeoff angle, and a 100 μm beam size. AFM samples were prepared by deposition from DMF onto a freshly cleaved mica surface. AFM samples were obtained using tapping mode. Length analysis of the SWNTs was performed with the AFM images using SIMAGIS Nanotechnology software version 3.0. TEM samples were prepared by deposition from water onto a Pelco200 lacey carbon grid (Product #01811). Sonication was carried out using a Cole-Palmer ultrasonic cleaner (Model #08849-00).

Repetitive Functionalization General Method. To a 500 mL flask was added 200 mL of a solution of **1** at a concentration of 60 mg/L (0.012 g, 1 mequiv of C). The mixture was stirred at room temperature while the aryl diazonium salt (2.0 mmol) was added as a solid. The solution was then adjusted to pH 10 using 1 M NaOH. Once the solution was at pH 10, it was allowed to stir at room temperature for 1 h. Workup involved diluting with acetone and filtering over a 1 μm polycarbonate filter. The resulting bucky paper was then washed with water and acetone to remove any impurities. Diazonium salts **2**−**9** were prepared as previously described from the appropriate aniline.[18]

General US-SWNT Formation Process.[13] To 0.100 g of purified HiPco SWNTs in a 100 mL round-bottom flask equipped with a stir bar under an N_2 atmosphere was added oleum (20% free SO_3, 25 mL). The material was stirred overnight to achieve a good dispersion. After dispersion, a mixture of oleum (25 mL) and concentrated nitric acid (18 mL) was slowly added. After complete addition the flask was transferred to an oil bath preheated to the desired temperature and heated for 2 h. The solution was carefully poured over ice (200 g) and filtered over a 1 μm polycarbonate filter. The resultant cake was washed on the filter thoroughly with water followed by ether. The cake was then dried in vacuo. *This process uses a highly reactive mixture of acids; strong exothermic*

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reactions are possible. Extreme caution should be used during the procedure. All cutting reactions should be done in a fume hood and appropriate safety equipment should be worn, including a lab coat, thick rubber gloves, safety glasses, and a full face and neck shield. An alternative workup consisted of first vacuum filtering over a 0.22 μm polycarbonate membrane and rinsing the filter cake thoroughly with water. The vacuum was then disconnected from the side arm and a minimal amount of methanol was added to the glass funnel to re-suspend the SWNTs. Ether was then added to the SWNT/methanol suspension to cause the SWNTs to precipitate. The vacuum was again applied and ether was continually added until the pH of the filtrate was neutral, at which point the filter cake was dried.

PEGylation General Procedure. US-SWNTs (0.050 g, 4.0 mequiv of C) were added to a 100 mL round-bottom flask equipped with a stir bar. To this was added dry DMF (50 mL) and the mixture was sonicated for 15 min to achieve dispersion. After dispersion, DCC (0.87 g, 4.2 mmol) was added and the mixture was allowed to stir 5 min before amine-terminated PEG (5000 MW, 1.04 g) was added. The mixture was allowed to stir 24 h at which point it was transferred to a dialysis bag (CelluSep H1, 50,000 MWCO, Part #: 1-5050-34, Membrane Filtration Products) and dialyzed in flowing water for 5 d to remove any unbound PEG. After dialysis, the material was filtered through glass wool to remove precipitated DCU. The concentration of the resultant material was then determined by Beer's law analysis using an extinction coefficient of 0.043 at lambda max 763 nm.

Dialysis Continuous Flow Setup. A deionized water spout was split into five separate lines using polypropylene T-joints and Nalgene tubing ($^5/_{16}$ in. i.d.). Each line was fed to the bottom of five separate 5 L beakers and the beakers were placed in a plastic tray (40 in. length × 24 in. width × 3 in. height) fitted with three drains at one end. The tray was slightly elevated at one end to promote drainage. The water source was turned on and the beakers were allowed to continually overflow. The flow rate was adjusted to prevent overflowing the tray.

4-Chloro-3-sulfonylphenyl SWNTs (1).[1] Purified SWNTs (0.250 g, 20.8 mequiv of C) were dispersed in oleum (250 mL, 20% free SO_3) with magnetic stirring for 3 h. Sodium nitrite (2.87 g, 41.6 mmol) was added followed by 4-chloroaniline (5.31 g, 41.6 mmol) and azobisisobutyronitrile (AIBN) (0.69 g, 4.2 mmol). The mixture was stirred at 80 °C for 1 h and then *carefully* poured over ice (250 g) and the suspension was filtered through a polycarbonate membrane (1 μm). The filter cake was washed with water and acetone. The resultant solid was then dispersed in dimethylformamide (DMF) and filtered over a polytetrafluoroethylene (PTFE) membrane (1 μm). The filter cake was washed with a copious amount of acetone and then dried to yield **1** (0.41 g, 320 mg/L). Raman D/G ratio 0.38; TGA mass loss 29%; XPS atomic concentration C 1s 76.30%, N 1s 2.94%, O 1s 15.81%, S 2p 2.69%, Cl 2p 2.27%.

4-*tert*-Butylphenyl/4-chloro-3-sulfonylphenyl SWNTs (10). The general method for repetitive functionalization was followed. 4-*tert*-Butylbenzenediazonium tetrafluoroborate (0.50 g, 2.0 mmol) was added to the SWNT solution. The final bucky paper (13 mg) was formed by filtering over a 0.2 μm PTFE filter and drying in vacuo. Raman D/G 0.55, TGA mass loss 35%. TGA analysis estimates 1/20 SWNT carbons functionalized. C 1s 86.1%, N 1s 1.7%, O 1s 9.1%, S 2p 1.6%, Cl 2p 1.4%.

4-Benzoic Acid/4-chloro-3-sulfonylphenyl SWNTs (11). The general method for repetitive functionalization was followed. 4-Benzoic acid diazonium tetrafluoroborate (0.47 g, 2.0 mmol) was added to the SWNT solution. The final bucky paper (15 mg) was formed by filtering over 0.2 μm PTFE filter and was dried in vacuo. Raman D/G 0.58, TGA mass loss 31%. TGA analysis estimates 1/20 SWNT carbons functionalized. C 1s 72.0%, N 1s 2.3%, O 1s 20.1%, S 2p 3.7%, Cl 2p 1.8%.

4-Methylbenzoate/4-chloro-3-sulfonylphenyl SWNTs (12). The general method for repetitive functionalization was followed. 4-Methyl benzoatediazonium tetrafluoroborate (0.50 g, 2.0 mmol) was added to the SWNT solution. The final bucky paper (10 mg) was formed by filtering over 0.2 μm PTFE filter and dried in vacuo. Raman D/G 0.76, TGA mass loss 40%. TGA analysis estimates 1/25 SWNT carbons functionalized. C 1s 77.3%, N 1s 1.3%, O 1s 18.23%, S 2p 1.6%, Cl 2p 1.5%.

4-Nitrophenyl/4-chloro-3-sulfonylphenyl SWNTs (13). The general method for repetitive functionalization was followed. 4-Nitrobenzenediazonium tetrafluoroborate (0.50 g, 2.0 mmol) was added to the SWNT solution. The final bucky paper (13 mg) was formed by filtering over a 0.2 μm PTFE filter and was dried in vacuo. Raman D/G 0.65, TGA mass loss 36%. TGA analysis estimates 1/21 SWNT carbons functionalized; XPS atomic concentration C 1s 76.4%, N 1s 5.5%, O 1s 15.0%, S 2p 1.6%, Cl 2p 1.5%.

4-Fluorophenyl/4-chloro-3-sulfonylphenyl SWNTs (14). The general method for repetitive functionalization was followed. The final bucky paper (14 mg) was formed by filtering over a 0.2 μm PTFE filter and was dried in vacuo. Raman D/G ratio 0.65; TGA mass loss 23%; TGA analysis estimates 1/27 SWNT carbons functionalized; XPS atomic concentration C 1s 67.59%, N 1s 4.00%, O 1s 24.15%, S 2p 1.17%, F 1s 3.09%.

4-Chlorophenyl/4-chloro-3-sulfonylphenyl SWNTs (15). The general method for repetitive functionalization was followed. The final bucky paper (12.4 mg) was formed by filtering over a 0.2 μm PTFE filter and was dried in vacuo. Raman D/G ratio 0.58; TGA mass loss 34%; TGA analysis estimates 1/18 SWNT carbons functionalized; XPS atomic concentration C 1s 80.55%, N 1s 1.65%, O 1s 10.48%, S 2p 1.26%, Cl 2p 5.95%, F 1s 0.00%.

4-Bromophenyl/4-chloro-3-sulfonylphenyl SWNTs (16). The general method for repetitive functionalization was followed. The final bucky paper (14 mg) was formed by filtering over a 0.2 μm PTFE filter and was dried in vacuo. Raman D/G ratio 0.62; TGA mass loss 43%; TGA analysis estimates 1/17 SWNT carbons functionalized; XPS atomic concentration C 1s 82.11%, N 1s 0.93%, O 1s 10.74%, S 2p 1.24%, Cl 2p 1.32%, Br 3d 3.63%, F 1s 0.03%.

4-Iodophenyl/4-chloro-3-sulfonylphenyl SWNTs (17). The general method for repetitive functionalization was followed. The final bucky paper (22.2 mg) was formed by filtering over a 0.2 μm PTFE filter and was dried in vacuo. Raman D/G ratio 0.63; TGA mass loss 53%. TGA analysis estimates 1/15 SWNT carbons functionalized; XPS atomic concentration C 1s 78.53%, N 1s 5.09%, O 1s 10.79%, S 2p 0.75%, Cl 2p 0.72%, I 4.12%, F 1s 0.00%.

US-SWNTs (18).[13,14] The general SWNT cutting procedure was followed with heating at 30 °C to yield **18** (0.110 g). Raman D/G ratio 0.65; TGA mass loss 49%. Average SWNT length 98 nm, as determined by AFM.

US-SWNTs (19). The general SWNT cutting procedure was followed with heating at 40 °C to yield **19** (0.094 g). Raman D/G ratio 0.58; TGA mass loss 49%. Average SWNT length 33 nm, as determined by AFM.

US-SWNTs (20). The general SWNT cutting procedure was followed with heating at 50 °C to yield **20** (0.102 g). Raman D/G ratio 0.89; TGA mass loss 55%. Average SWNT length 33 nm, as determined by AFM.

US-SWNTs (21). The general SWNT cutting procedure was followed with heating at 60 °C to yield **21** (0.202 g). Raman D/G ratio 0.92; TGA mass loss 54%. Average SWNT length 34 nm, as determined by AFM.

US-SWNTs (22). The general SWNT cutting procedure was followed with heating at 70 °C to yield **22** (0.203 g). Raman D/G ratio 0.94; TGA mass loss 63%. Average SWNT length 32 nm, as determined by AFM.

PEGylated US-SWNTs (23). The PEGylation general procedure was followed using **18** as starting SWNT material to yield **23** (concentration 160 mg/L); Raman D/G 0.44; TGA mass loss 71%; XPS atomic concentration C 1s 65.9%, N 1s 3.4%, O 1s 30.3%, S 2p 0.2%, Br 3d 0.2%, I 3d5 0.0%, F 1s 0.0%, Cl 2p 0.0%.

PEGylated US-SWNTs (24). The PEGylation general procedure was followed using **19** as starting SWNT material to yield **24** (concentration 77 mg/L).

PEGylated US-SWNTs (25). The PEGylation general procedure was followed using **20** as starting SWNT material to yield **25** (concentration 32 mg/L).

PEGylated US-SWNTs (26). The PEGylation general procedure was followed using **21** as starting SWNT material to yield **26** (concentration 19 mg/L).

PEGylated US-SWNTs (27). The PEGylation general procedure was followed using **22** as starting SWNT material to yield **27** (concentration 14 mg/L).

4-Nitrophenyl PEGylated US-SWNTs (28). The general method for repetitive functionalization was followed using **23** as the starting PEGylated SWNTs material to give **28**. Raman D/G 0.53; TGA mass loss 51%;[19] XPS atomic concentration C 1s 67.7%, N 1s 7.0%, O 1s 24.8%, S 2p 0.2%.

4-Fluorophenyl PEGylated US-SWNTs (29). The general method for repetitive functionalization was followed using **23** as the starting PEGylated SWNTs material to give **29**. Raman D/G 0.62; TGA mass loss 53%;[19] XPS atomic concentration C 1s 72.2%, N 1s 6.3%, O 1s 17.4%, S 2p 0.1%, F 1s 4.0%.

4-Chlorophenyl PEGylated US-SWNTs (30). The general method for repetitive functionalization was followed using **23** as the starting PEGylated SWNTs material to give **30**. Raman D/G 0.75; TGA mass loss 59%;[19] XPS atomic concentration C 1s 71.9%, N 1s 4.1%, O 1s 19.4%, S 2p 0.4%, Cl 2p 4.1%.

4-Iodophenyl PEGylated US-SWNTs (31). The general method for repetitive functionalization was followed using **23** as the starting PEGylated SWNTs material to give **31**. Raman D/G 0.82; TGA mass loss 58%.[12] XPS atomic concentration C 1s 61.4%, N 1s 8.4%, O 1s 28.1%, S 2p 0.1%, I 3d5 0.7%.

Biotin [4-(2-aminoethoxy)phenyl](3,3-diethyl)triazene Amide (32). A previously published procedure was used.[10]

Biotin [4-(2-aminoethoxy)phenyl](3,3-diethyl)triazene Amide PEGylated US-SWNTs (33). The general method for repetitive functionalization was followed by adding **32** to the PEGylated SWNT **23** (a different lot of **23** was used with a D/G of 0.26) and adjusting the pH to 2 with 6 M HCl. After the mixture was stirred for 5 min, the pH was adjusted to 10 with 6 M NaOH. The reaction was stirred for 12 h at room temperature to give **33**. Raman D/G 0.43; TGA mass loss 65%. XPS atomic concentration C 1s 83.8%, N 1s 1.0%, O 1s 15.1%.

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[19] Lower TGA weight losses from the multifunctional US-SWNTs could be attributed to thermal stabilization of the systems.