JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

Analysis of Functionalization Degree of Single-Walled Carbon Nanotubes Having Various Substituents

Yutaka Maeda,*[†] Kazuma Saito,[†] Norihisa Akamatsu,[†] Yuriko Chiba,[†] Seina Ohno,[†] Yumi Okui,[†] Michio Yamada,[†] Tadashi Hasegawa,[†] Masahiro Kako,[‡] and Takeshi Akasaka*[§]

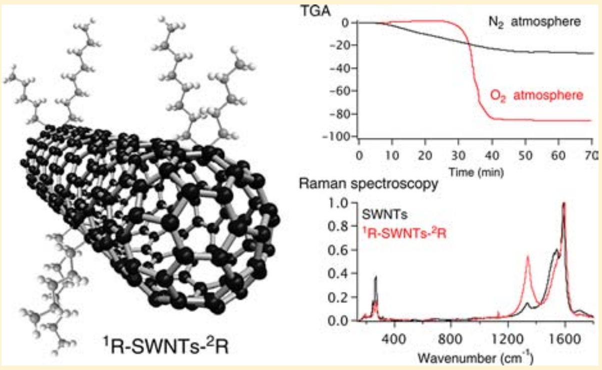
[†]Department of Chemistry, Tokyo Gakugei University, Tokyo 184-8501, Japan

[‡]Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan

[§]Life Science Center of Tsukuba Advanced Research Alliance, University of Tsukuba, Ibaraki 305-8577, Japan

Supporting Information

ABSTRACT: Introducing substituents onto SWNT sidewalls increases their solubility and tunes their properties. Controlling the degree of functionalization is important because the addition of numerous functional groups on the sidewall degrades their intrinsic useful electronic properties. We examined the synthesis and characterization of sidewall-functionalized SWNTs in this study. The functionalized SWNTs (^{1}R-SWNTs-^{2}R) were prepared in a one-pot reaction of SWNTs with alkyllithium (^{1}RLi) followed by alkyl bromide (^{2}RBr). The functionalized SWNTs were characterized by the absorption and Raman spectroscopy and thermogravimetric analysis. Not only the total number of functional groups introduced on the SWNT sidewall (formula mass: ^{1}R = ^{2}R) but also the ratio of ^{2}R to ^{1}R in the functionalized SWNTs (formula mass: ^{1}R ≠ ^{2}R) having two different substituents were clarified using the relation between results of Raman spectroscopy and thermogravimetric analysis. Results show that the degree of functionalization of ^{2}R to ^{1}R in ^{1}R-SWNTs-^{2}R can be well controlled by the bulkiness of the alkyl groups of ^{1}RLi and ^{2}RBr. Moreover, substituent effects of reductive alkylation and reductive silylation of SWNTs via Birch reduction were investigated.



■ INTRODUCTION

Single-walled carbon nanotubes (SWNTs) have attracted broad attention because of their outstanding mechanical and electronic properties, which have given rise to many potential applications.[1−3] Because of the low dispersibility of SWNTs in aqueous and organic solvents, several dispersion procedures have been developed.[4−7] Much attention has been devoted to the introduction of functional groups onto the SWNT sidewall because the groups affect not only the increase of solubility but also the change of electrochemical properties of SWNTs.[8−11] For example, silylation of SWNTs increases field emission properties of SWNTs and enhances the n-type properties of field effect transistors.[12−14] In contrast, SWNTs lose their outstanding electronic properties by excessive functionalization because of partial disconnection of the π-conjugated systems.[15,16] Consequently, it is important to control the degree of functionalization of the SWNT sidewall.

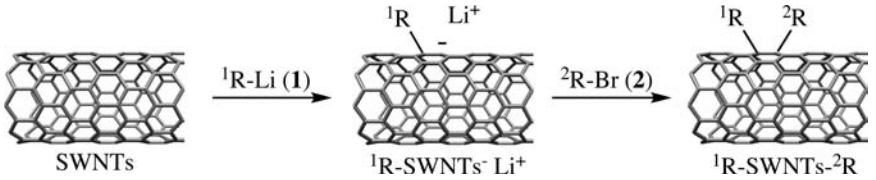
Reductive alkylation of SWNTs has been conducted widely for the introduction of functional groups onto the SWNT sidewall.[17−25] This reductive alkylation reportedly proceeds effectively. The bundles of SWNT are well exfoliated by the repulsion of SWNT anion intermediates produced in the reaction. Recently, two-step reductive alkylation of SWNTs using alkyllithium and alkyl halide has been reported.[26] The two-step reductive alkylation showed significant substituent effects on the degree of functionalization.[27] The degree of functionalization can be controlled by the substituents of alkyllithium and alkyl halide. The controlled multiple functionalization of SWNTs is now a challenging subject for practical applications.[28−32]

Absorption and Raman spectroscopy and thermogravimetry (TG) are currently the most powerful methods used to study the degree of functionalization on SWNTs.[18,33] Haddon et al. reported details of characteristic absorption and the Raman spectra change accompanied by an increase of the degree of sidewall functionalization.[33,34] The degree of functionalization is estimated on the basis of the intensity ratio of the D band to the G band (D/G ratio: [D/G]). The degree of functionalization, which is defined as the number of SWNT carbon atoms per functional group (functional group coverage: FGC), is determined from the weight losses in TGA.[18,30] Substituents having the same formula mass are required for the estimation of FGC of functionalized SWNTs. Unfortunately, functionalization degree is not clarified for each substituent in the multi-

Received: August 10, 2012
Published: October 11, 2012

dx.doi.org/10.1021/ja308969p | *J. Am. Chem. Soc.* 2012, 134, 18101−18108

Scheme 1



functionalized SWNTs using absorption and Raman spectroscopy and thermogravimetry, independently.

For this study, we prepared functionalized SWNTs using butyllithium and alkyl bromide, and estimated the degree of functionalization in two-step alkylation. A good relation between [D/G] obtained from the Raman spectra and $\mathrm{FGC_{exp}}$ determined from TGA was found in Bu-SWNTs-Bu. Moreover, on the basis of the relation between [D/G] and FGC of Bu-SWNTs-Bu, the functionalization ratio of ^{2}R to ^{1}R in ^{1}R-SWNTs-^{2}R ($^2\mathrm{R} \neq \mathrm{Bu}$) was revealed by analyses of ^{1}R-SWNTs-^{2}R having different substituents. In addition, substituent effects on the reductive alkylation and silylation of SWNTs via Birch reduction were investigated.

■ EXPERIMENTAL SECTION

SWNTs (HiPco SWNTs) were obtained from Unidym Inc.: SWNTs (Lot No. P2150) were used for the two-step alkylation; SWNTs (Lot No. R0513) were used for the reductive alkylation and silylation of SWNTs via Birch reduction. The solution-phase visible-near-infrared (vis−NIR) absorption spectra were recorded using a spectrophotometer (V-670; Jasco Corp.) with a Pyrex cell of 10 mm path length. Raman spectra were measured using a spectrophotometer (LabRAM HR-800; Horiba Ltd.) with excitation wavelengths of 514.5 and 633 nm. Scanning electron microscope (SEM) observation was conducted using a field-emission electron microscope (15 kV accelerating voltage, 20 mA beam current, S4500; Hitachi Ltd.). TGA was performed at a heating rate of 10 °C/min and a nitrogen flow rate of 400 mL/min or an air flow rate of 100 mL/min (Thermo plus TG8120; Rigaku). Ultrasound irradiation was performed using a bath sonicator (B2510J-MT ultrasonic cleaner; Branson).

Two-Step Alkylation of SWNTs. Into a 100-mL heat-dried, three-necked, round-bottom flask were placed 8.0 mg of purified HiPco SWNTs and 80 mL of anhydrous benzene; this mixture was then sonicated for 30 min under argon. To this dispersion was added 3.2 mL of 1.6 M solution of butyllithium (**1**, 5.1 mmol) in pentane. After the resulting suspension of an alkylated SWNTs anion (Bu-SWNTs-Li$^+$) was stirred for 30 min, it was sonicated for 30 min. Then butyl bromide (**2**, 10.2 mmol) was added to the mixture. The mixture was stirred for 1 h and then quenched by addition of 20 mL of dry ethanol. The reaction mixture was washed with water and diluted in 1.0 M hydrochloric acid until the pH value remained neutral. The suspended black solid was collected by filtration using a membrane filter (PTFE, 1.0 mm) and washed with tetrahydrofuran, methanol, and dichloromethane using the dispersion−filtration process. The solid was dried under vacuum at 50 °C. SWNTs and functionalized SWNTs were dispersed in tetrahydrofuran containing 1.0 M propylamine.[35] The dispersion liquid was used for absorption spectra measurements.

D band intensity reflects not only the defect density on the sidewalls of SWNTs but also the amount of impurity particles. HiPco SWNTs were used in this study in order to greatly reduce the influence of impurity particles, such as amorphous carbon. SEM images and TGA of the HiPco SWNTs used did not show any obvious impurity. The information of chiral selectivity in the reaction can be evaluated due to wide chirality distribution of HiPco SWNTs. There is an additional advantage because it can be compared with the results reported previously.

$\mathrm{FGC_{exp}}$ was estimated from the wt% of the functional groups ($\mathrm{wt\%_{sub}}$) and SWNTs ($\mathrm{wt\%_{SWNTs}}$) in ^{1}R-SWNTs-^{2}R and the molecular weights of the functional groups (M_{wsub}) and atomic mass of carbon according to the following equation (eq 1).

$$\mathrm{FGC_{exp}} = \frac{\mathrm{wt\%_{SWNTs}}/12.01}{\mathrm{wt\%_{sub}}/\mathrm{Mw_R}} \qquad (1)$$

The $\mathrm{wt\%_{sub}}$ was determined from the mass loss from TGA at 800 °C in $\mathrm{N_2}$ atmosphere according to the previously reported method.[18,30] The $\mathrm{wt\%_{SWNTs}}$ was determined from the mass loss of the residual materials, ^{1}R-SWMTs-^{2}R after TGA in $\mathrm{N_2}$, at 800 °C in air atmosphere.

The ratios of ^{2}R to ^{1}R (^{2}R/^{1}R) of Bu-SWNTs-^{2}R were estimated according to the following equation (eq 2). $\mathrm{Wt\%_{sub}}$ and $\mathrm{wt\%_{SWNTs}}$ in Bu-SWNTs-^{2}R were obtained using TGA. Calculated FGC ($\mathrm{FGC_{cal}}$) was estimated from $[\mathrm{D/G}]_{514.5\ \mathrm{nm}}$ of Bu-SWNTs-^{2}R using the relation between $[\mathrm{D/G}]_{514.5}$ and $\mathrm{FGC_{exp}}$ of Bu-SWNTs-Bu as shown in Figure 4.

$$\chi = \frac{\mathrm{wt\%_{Sub}}\cdot\mathrm{FGC_{cal}}\cdot 12.01}{\mathrm{wt\%_{SWNTs}}(\mathrm{Mw}_{^1\mathrm{R}} - \mathrm{Mw}_{^2\mathrm{R}})} = \frac{\mathrm{Mw}_{^2\mathrm{R}}}{(\mathrm{Mw}_{^1\mathrm{R}} - \mathrm{Mw}_{^2\mathrm{R}})}$$

$$\mathrm{Mw_{sub}} = \chi\cdot\mathrm{Mw}_{^1\mathrm{R}} + (1-\chi)\cdot\mathrm{Mw}_{^2\mathrm{R}}$$

$$(^1\mathrm{R} \neq {}^2\mathrm{R})$$

$$(^2\mathrm{R}/^1\mathrm{R}) = \frac{1-\chi}{\chi} \qquad (2)$$

Reductive Alkylation and Silylation of SWNTs via Birch Reduction. In a heat-dried, 50-mL, three-necked flask, were placed 8 mg of HiPco SWNTs, 4,4′-di-*tert*-butylbiphenyl (DTBP) (160 mg, 0.6 mmol), and 32 mL of anhydrous tetrahydrofuran. The mixture was sonicated and dispersed under argon atomsphere. The dispersion was added to lithium (138.8 mg, 6 mmol) in a heat-dried, 100 mL, three-necked flask under argon atmosphere. The mixture was sonicated for 60 min. The color of the mixture became green, indicating formation of the DTBP anion radical from DTBP. Alkyl bromide (**2**, 6 mmol) was added to the reaction mixture. The mixture was sonicated for 30 min and then quenched with ethanol. The reaction mixture was washed with 1.0 M hydrochloric acid and water until the pH value remained neutral. The suspended black solid was collected by filtration using a membrane filter (PTFE, 0.1 mm) and washed with dichloromethane, methanol, and tetrahydrofuran. The solid was dried under vacuum at 50 °C. For comparison of absorption spectra under the same conditions, SWNTs and functionalized SWNTs were dispersed in tetrahydrofuran containing 1.0 M propylamine and used for spectral analysis. Propylamine is used as a dispersant reagent for SWNTs because of the low dispersibility of the starting SWNTs.

Synthetic Procedure of (3-Bromopropoxy)-*tert*-butyldimethylsilane. A mixture of 3-bromopropanol (2.6 mL, 18 mmol), imidazole (3.7 g, 54 mmol), and *tert*-butyldimethylsilylchloride (TBDMS-Cl) (4.7 g, 31 mmol) in anhydrous THF (50 mL) was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was diluted with water and extracted three times with dichloromethane. The organic layers were combined, washed with brine, dried, and evaporated to obtain (3-bromopropoxy)-*tert*-butyldimethylsilane in quantitative yield.

(3-Bromopropoxy)-*tert*-butyldimethylsilane: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 0.06$ (s, 6H, Si−$\mathrm{CH_3}$); 0.89 (s, 9H, C−$\mathrm{CH_3}$); 2.03 (m, 2H, $\mathrm{CH_2}$); 3.51 (t, $J = 6.4$ Hz 2H, Br−$\mathrm{CH_2}$); 3.73 (t, $J = 5.7$ Hz, 2H, −$\mathrm{CH_2}$−O). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = -5.3$ (Si−$\mathrm{CH_3}$); 18.4 ($\underline{\mathrm{C}}$−$\mathrm{Me_3}$); 26.0 (C−$\underline{\mathrm{C}}\mathrm{H_3}$); 30.8 (−$\mathrm{CH_2}$−); 35.6 (Br−$\mathrm{CH_2}$); 60.5 (−$\mathrm{CH_2}$−O).

(3-Bromo-2,2-dimethylpropyloxy)-*tert*-butyldimethylsilane: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 0.00$ (s, 6H, Si−$\mathrm{CH_3}$); 0.85 (s, 9H,

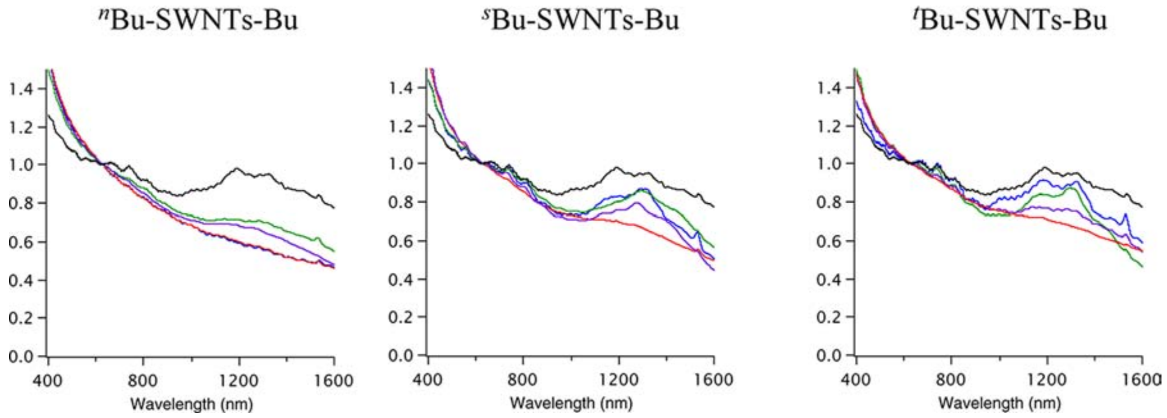


Figure 1. Absorption spectra of Bu-SWNTs-Bu in THF solution containing propylamine normalized at 628 nm. SWNTs (black), ^{2}R: ^{n}Bu (red), ^{i}Bu (purple), ^{s}Bu (green), and ^{t}Bu (blue).

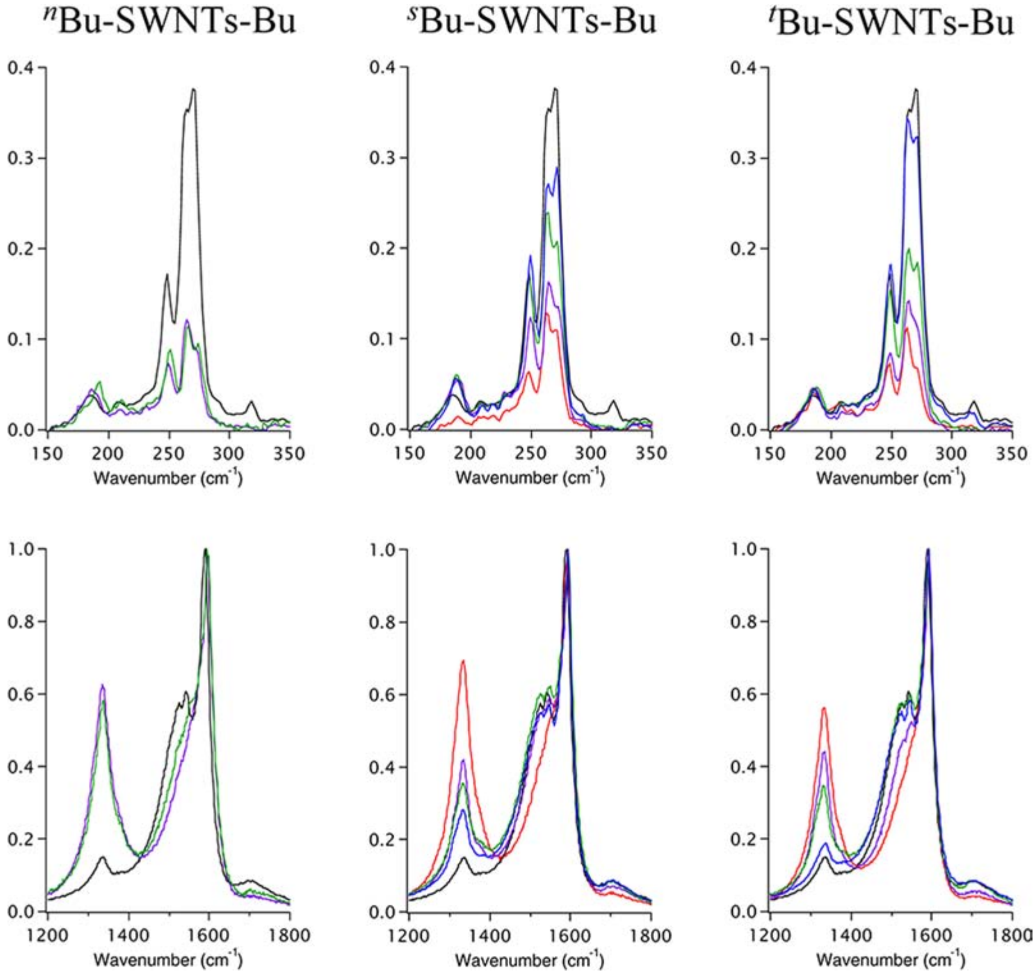


Figure 2. Raman spectra of Bu-SWNTs-Bu normalized at the G band with excitation wavelengths 514.5 nm. SWNTs (black); ^{2}R = ^{n}Bu (red); ^{2}R = ^{i}Bu (purple); ^{2}R = ^{s}Bu (green); and ^{2}R = ^{t}Bu (blue).

$C{-}CH_3$); 0.92 (s, 6H, $C{-}CH_3$); 3.30 (s, 2H, $Br{-}CH_2$); 3.32 (s, 2H, $-CH_2{-}O$). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -5.4$ ($Si{-}CH_3$); 18.2 ($\underline{C}{-}Me_3$); 23.0 ($-C{-}(\underline{C}H_3)_2$); 25.9 ($C{-}(\underline{C}H_3)_3$); 36.9 ($-\underline{C}{-}(CH_3)_2$); 43.3 ($Br{-}CH_2$); 67.9 ($-CH_2{-}O$).

■ RESULTS AND DISCUSSION

Functionalization of SWNTs was achieved using the reaction with alkyllithium (^{1}RLi, **1**) followed by alkyl bromide (^{2}RBr, **2**) under argon according to the literature.[27] (Scheme 1) Bu-SWNTs-Bu was confirmed using absorption and Raman spectra. The intensities of the characteristic absorptions in the absorption spectra of Bu-SWNTs-Bu decreased remarkably (Figure 1), which indicates that sidewall functionalization occurred. Figure 2 shows the Raman spectra of Bu-SWNTs-Bu measured at 514.5 nm excitation. The order of $[D/G]_{514.5\ nm}$ in ^{1}R-SWNTs-^{n}Bu is: ^{n}Bu-SWNTs-^{n}Bu < ^{s}Bu-SWNTs-^{n}Bu < ^{t}Bu-SWNTs-^{n}Bu, as presented in Table 1. The highest $[D/G]_{514.5\ nm}$ value of ^{t}Bu-

Table 1. D/G Ratio ($[D/G]_{514.5\ nm}$) and TGA-Determined wt % of Substituent (wt$\%_{sub}$) and Functional Group Coverage (FGC_{exp}) of Bu-SWNTs-Bu

^{1}R-SWNTs-^{2}R	$[D/G]_{514.5\ nm}$	wt% of substituent	FGC_{exp}
^{n}Bu-SWNTs-^{n}Bu	0.64	15.9	25.1
^{n}Bu-SWNTs-^{i}Bu	0.60	13.4	30.8
^{n}Bu-SWNTs-^{s}Bu	0.58	13.2	31.2
^{n}Bu-SWNTs-^{t}Bu	0.75	17.2	22.9
^{s}Bu-SWNTs-^{n}Bu	0.70	15.7	25.6
^{s}Bu-SWNTs-^{i}Bu	0.42	12.1	34.6
^{s}Bu-SWNTs-^{s}Bu	0.36	11.2	37.7
^{s}Bu-SWNTs-^{t}Bu	0.28	9.90	43.1
^{t}Bu-SWNTs-^{n}Bu	0.71	16.0	25.0
^{t}Bu-SWNTs-^{i}Bu	0.44	12.4	33.6
^{t}Bu-SWNTs-^{s}Bu	0.35	11.2	37.8
^{t}Bu-SWNTs-^{t}Bu	0.19	9.10	47.6

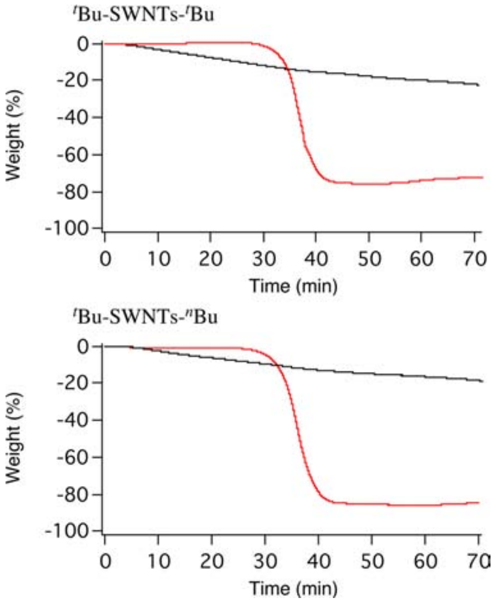


Figure 3. TG curves of ^{t}Bu-SWNTs-Bu from 100 to 800 °C at a heating rate of 10 °C/min in N_2 atmosphere (black). TG curves of the residual materials, ^{t}Bu-SWNTs-Bu after TGA in N_2 atmosphere, from 100 to 800 °C at a heating rate of 10 °C/min in air atmosphere (red).

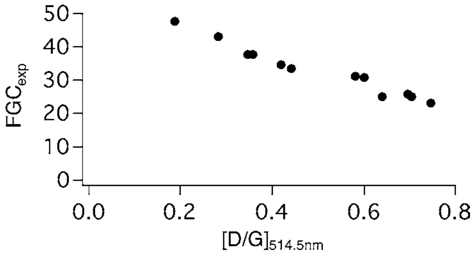


Figure 4. $[D/G]_{514.5\ nm}$ of Bu-SWNTs-Bu as a function of FGC_{exp}.

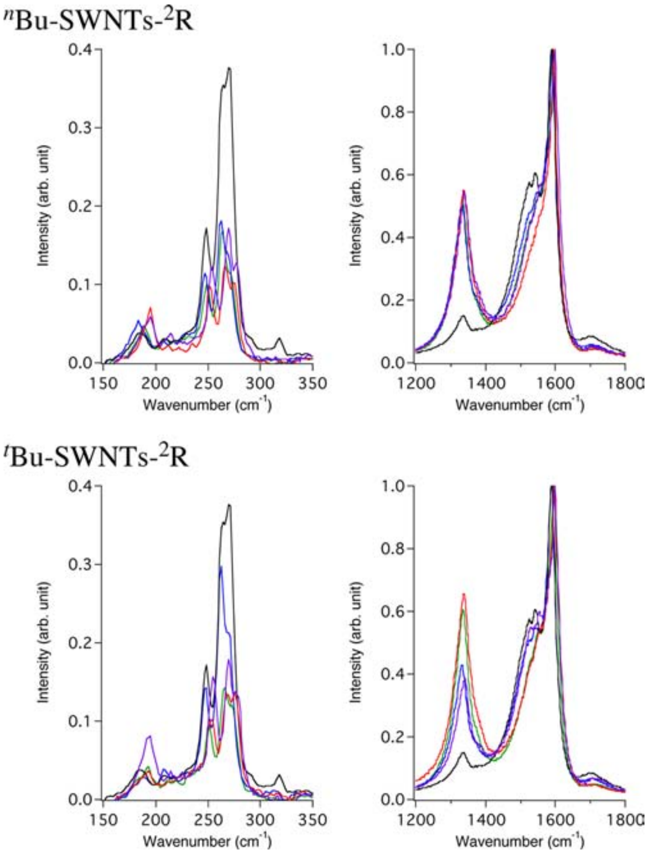


Figure 5. Raman spectra of ^{1}R-SWNTs-^{2}R normalized at the G band with excitation wavelengths 514.5 nm. SWNTs (black); ^{2}R = ^{n}octyl (red); ^{2}R = ^{n}dodecyl (green), ^{n}octadecyl (blue); ^{2}R = ^{s}octyl (purple).

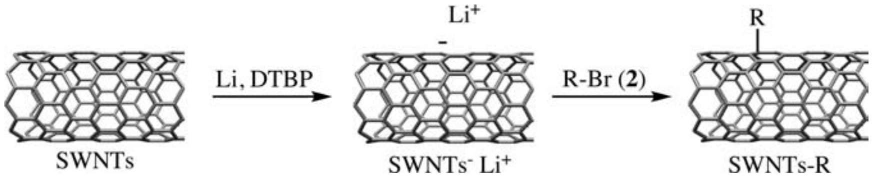
Table 2. D/G Ratio ($[D/G]_{514.5\ nm}$), wt% of Substituent (wt $\%_{sub}$), FGC_{cal}, and Ratio of ^{2}R to ^{1}R (^{2}R/^{1}R) of ^{1}R-SWNTs-^{2}R

^{1}R-SWNTs-^{2}R	$[D/G]_{514.5\ nm}$	wt% of substituent	FGC_{cal}	^{2}R/^{1}R)
^{n}Bu-SWNTs-^{n}octyl	0.59	19.5	29.2	0.86
^{n}Bu-SWNTs-^{s}octyl	0.55	18.0	30.9	0.79
^{n}Bu-SWNTs-^{n}dodecyl	0.55	21.4	31.0	0.65
^{n}Bu-SWNTs-^{n}octadecyl	0.50	22.2	32.8	0.39
^{t}Bu-SWNTs-^{n}octyl	0.66	20.6	26.6	0.85
^{t}Bu-SWNTs-^{s}octyl	0.39	13.3	37.5	0.26
^{t}Bu-SWNT-^{n}dodecyl	0.59	23.0	29.2	0.74
^{t}Bu-SWNTs-^{n}octadecyl	0.43	14.5	35.8	0.09

SWNTs-^{n}Bu indicates that the reactivity of ^{t}BuLi to SWNTs, producing the ^{t}Bu-SWNTs- intermediate, is higher than those of other BuLi. It is particularly interesting that the order of $[D/G]_{514.5\ nm}$ in ^{t}Bu-SWNTs-^{2}R, ^{s}Bu-SWNTs-^{2}R, and ^{n}Bu-SWNTs-^{2}R is ^{1}R-SWNTs-^{t}Bu < ^{1}R-SWNTs-^{s}Bu < ^{1}R-SWNTs-^{i}Bu < ^{1}R-SWNTs-^{n}Bu. The exception is the order of the value of ^{n}Bu-SWNTs-^{t}Bu. We can safely conclude that the degree of functionalization is decreased with an increase of steric hindrance of ^{1}R and ^{2}R, and affected by ^{1}R stronger than ^{2}R. The unexpectedly high reactivity of ^{n}Bu-SWNTs-^{t}Bu might be attributable to the steric hindrance of the ^{t}Bu radical, which might prevent dimerization and disproportionation of ^{t}Bu radical and react with ^{n}Bu-SWNTs radical having curvature.

Analysis of the number of functional groups on the SWNTs was performed on the basis of TG under heating to 800 °C at a rate of 10 °C/min (Figure 3 and Figures S8–S10 in Supporting Information). From the observed weight loss, FGC of Bu-SWNTs-Bu (FGC_{exp}) was estimated as shown in Table 1. Both $[D/G]_{514.5\ nm}$ and FGC_{exp} imply the degree of functional of SWNTs. Therefore, FGC_{exp} is expected to be consistent with $[D/G]_{514.5\ nm}$. In fact, $[D/G]_{514.5\ nm}$ and FGC_{exp} show a linear relation, as portrayed in Figure 4.

Scheme 2



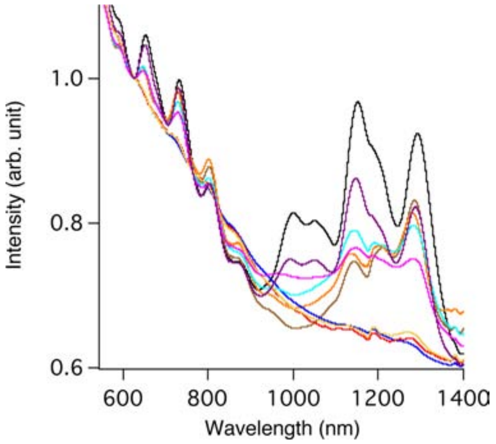


Figure 6. Absorption spectra of SWNTs and SWNTs-R. From top to bottom at 1151 nm: SWNTs (black), SWNTs-^{t}Bu (purple), SWNTs-neopentyl (aqua), SWNTs-Ph (pink), SWNTs-^{i}Pr (orange), SWNTs-CH_2Ph (brown), SWNTs-^{n}Bu (blue), SWNTs-CH_2CH_2Ph (yellow), and SWNTs-^{n}octyl (red).

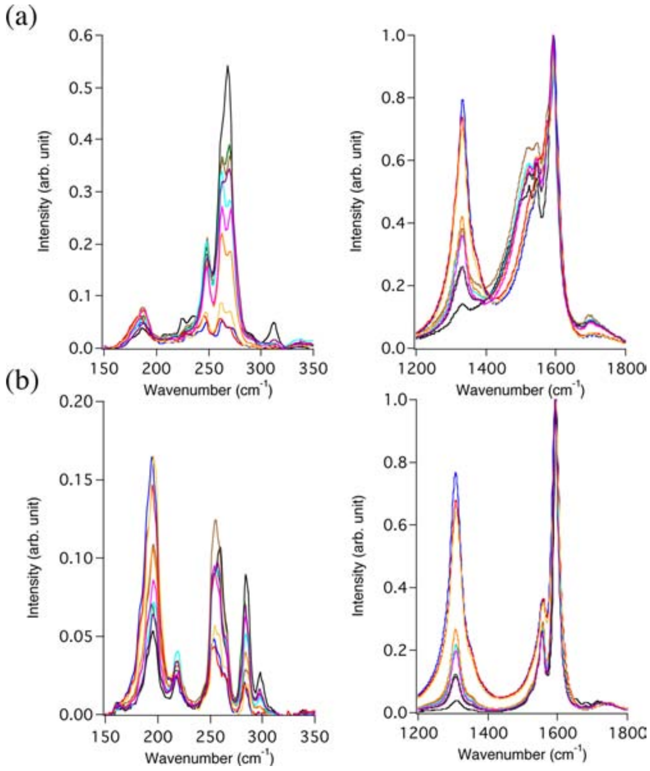


Figure 7. Raman spectra of SWNTs and SWNTs-R normalized at the G band. From top to bottom at 268 cm^{-1}: SWNTs, SWNTs-benzyl, SWNTs-^{t}Bu, SWNTs-neopentyl, SWNTs-Ph, SWNTs-^{i}Pr, SWNTs-phenethyl, SWNTs-^{n}Bu, and SWNTs-^{n}octyl. From top to bottom at the D band: SWNTs-^{n}Bu, SWNTs-^{n}octyl, SWNTs-phenethyl, SWNTs-^{i}Pr, SWNTs-neopentyl, SWNTs-benzyl, SWNTs-Ph, SWNTs-^{t}Bu, and SWNTs. Excitation wavelengths: (a) 514.5 nm. (b) 633 nm.

Table 3. D/G Ratios ($[D/G]_{514.5\ nm}$ and $[D/G]_{633\ nm}$) of SWNTs-R

SWNTs-R	$[D/G]_{514\ nm}$	$[D/G]_{633\ nm}$
SWNTs-^{n}Bu	0.79	0.77
SWNTs-^{n}octyl	0.73	0.67
SWNTs-phenethyl	0.71	0.64
SWNTs-^{i}Pr	0.42	0.27
SWNTs-benzyl	0.36	0.22
SWNTs-neopentyl	0.39	0.24
SWNTs-Ph	0.36	0.19
SWNTs-^{t}Bu	0.25	0.11
SWNTs-$SiMe_3$	0.39	0.24
SWNTs-$SiEt_3$	0.28	0.15

When the formula masses of ^{1}R and ^{2}R are equal, the presence of carbon atoms of SWNTs for one functional group on ^{1}R-SWNTs-^{2}R can be estimated using TGA, but no information about the ratio of the number of ^{2}R to that of ^{1}R in ^{1}R-SWNTs-^{2}R is obtainable. When the formula masses of ^{1}R and ^{2}R are not equal, the ratio of ^{2}R to ^{1}R of ^{1}R-SWNTs-^{2}R ($^{1}R \neq {}^{2}R$) can be estimated from comparison of the TGA weight loss and [D/G] value in ^{1}R-SWNTs-^{2}R ($^{1}R \neq {}^{2}R$) and that in Bu-SWNTs-Bu. To ascertain the ratio of ^{2}R to ^{1}R, functionalized SWNTs (^{1}R = Bu, $^{2}R \neq$ Bu) were prepared, and wt%'s of the functional groups, $[D/G]_{514.5\ nm}$, on Bu-SWNTs-^{2}R were evaluated. The degree of functionalization determined by $[D/G]_{514.5\ nm}$ in Bu-SWNTs-^{2}R decreased along with the increase of the alkyl chain length and bulkiness of ^{2}R (Figure 5). Consequently, the calculated FGC (FGC_{cal}) in Bu-SWNTs-^{2}R ($^{2}R \neq$ Bu) was estimated from the linear relation between $[D/G]_{514.5\ nm}$ and FGC_{exp} in Bu-SWNTs-Bu and $[D/G]_{514.5\ nm}$ of Bu-SWNTs-^{2}R ($^{2}R \neq$ Bu). The ratios of ^{2}R to ^{1}R ($^{2}R/^{1}R$) of Bu-SWNTs-^{2}R were estimated using eq 2 from $wt\%_{sub}$ and $wt\%_{SWNTs}$ in Bu-SWNTs-^{2}R and FGC_{cal}. (Table 2) It is particularly noteworthy that the $^{2}R/^{1}R$ in Bu-SWNTs-^{2}R shows the same tendency as the degree of functionalization determined using Raman spectroscopy. The degree of functionalization and the $^{2}R/^{1}R$ are strongly influenced respectively by the alkyl groups of ^{2}R and ^{1}R.

The substituent effects on the functionalization degree in the reductive alkylation of SWNTs via Birch reduction were studied. Alkylation of SWNTs was conducted according to the reported methods.[20] (Scheme 2) The intensity of the characteristic absorptions in the absorption spectra of SWNTs-Bu decreased remarkably (Figure 6), which indicates that sidewall functionalization took place. The relative functionalization degree of SWNTs-R estimated from the decrease of S_{11} bands is the following: SWNTs-^{n}Bu, SWNTs-^{n}octyl, SWNTs-^{n}phenethyl > SWNTs-^{i}Pr, SWNTs-benzyl, SWNTs-neopentyl, SWNTs-Ph > SWNTs-^{t}Bu. This order is consistent with that in the alkylation of ^{t}Bu-SWNTs-Li$^+$ with alkyl bromide.[27] Hirsch et al. studied the selectivity in the reaction of SWNTs-Na$^+$ with 1-iodobutane in ammonia at −78 °C. They reported that SWNTs with small

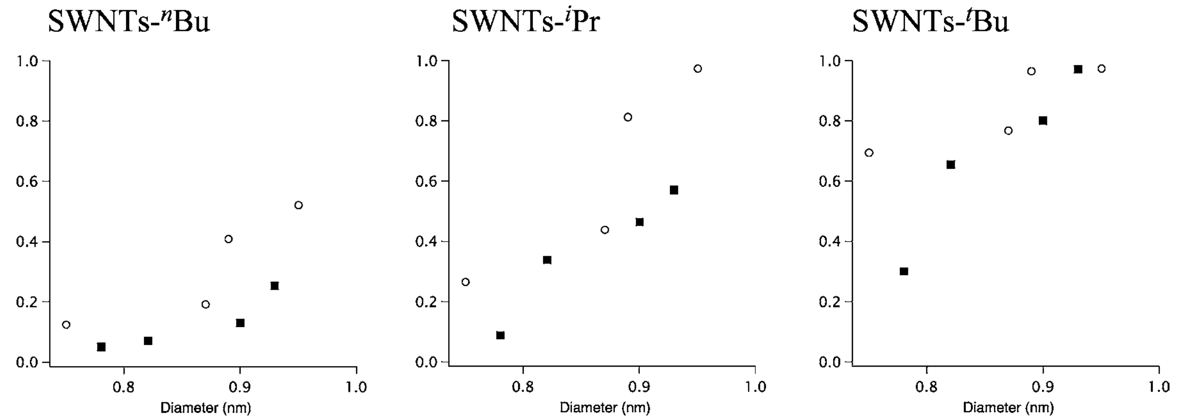
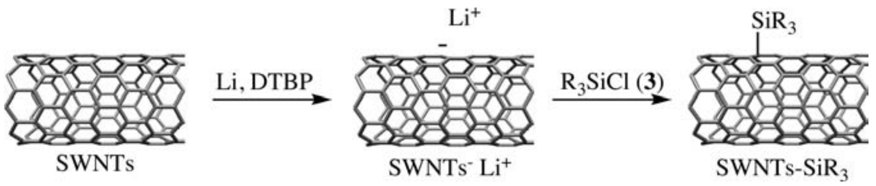


Figure 8. Relative RBM peak intensity of SWNTs-R toward that of pristine SWNTs. (○): semiconducting SWNTs; (■): metallic SWNTs.

Scheme 3



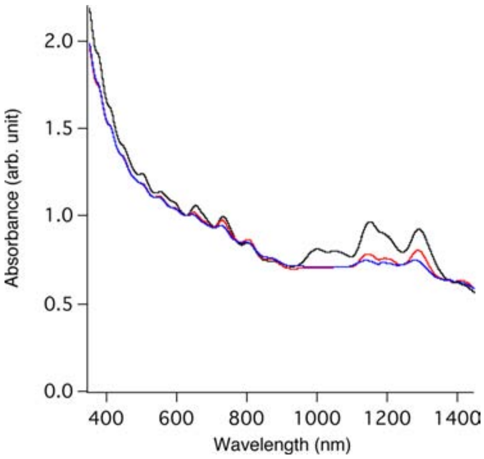


Figure 9. Absorption spectra of SWNTs-SiR$_3$ in THF solution containing propylamine normalized at 628 nm. SWNTs (black); R = Et (red); and R = Me (blue).

diameters were more reactive than those with larger diameters.[36] The diameters (d_t) of SWNTs used were estimated as 1.09, 1.00, 0.89, 0.81, and 0.78 nm from the equation $S_{11} = 0.962/d_t$.[37] The absorbance of SWNTs-^{i}Pr, SWNTs-benzyl, SWNTs-neopentyl, and SWNTs-^{t}Bu is markedly reduced in smaller-diameter SWNTs compared to larger-diameter SWNTs.

Figure 7 shows the Raman spectra of SWNTs-R. Table 3 shows D/G ratios for the functionalized SWNTs determined from the Raman spectra measured at 514.5 and 633 nm excitations. The relative degree of functionalization of SWNTs estimated from the D/G ratio is the following: SWNTs-^{n}Bu, SWNTs-^{n}octyl, SWNTs-^{n}phenethyl > SWNTs-^{i}Pr, SWNTs-benzyl, SWNTs-neopentyl, SWNTs-Ph > SWNTs-^{t}Bu, which is consistent with that estimated from the absorption spectra. To clarify the diameter selectivity in the reaction of SWNTs-Li$^+$ with **1**, the diameters of the SWNTs were estimated. The SWNT diameters were 1.27, 0.95 0.89, 0.87, and 0.75 nm (514.5 nm) and 1.22, 1.09, 0.93, 0.90, 0.82, and 0.78 nm (633 nm), from the equation $w_{\mathrm{RBM}} = Ad_t^{-1} + B$ ($A = 223.5\ \mathrm{cm}^{-1}$ and $B = 12.5\ \mathrm{cm}^{-1}$) where w_{RBM} is the wavenumber of RBM.[38−40] The amount of the decrease of relative peak intensity of SWNTs with small diameters was larger than those of large diameters, which also suggests that SWNTs with small diameters are considerably more reactive than SWNTs with large diameters. Figure 8 shows

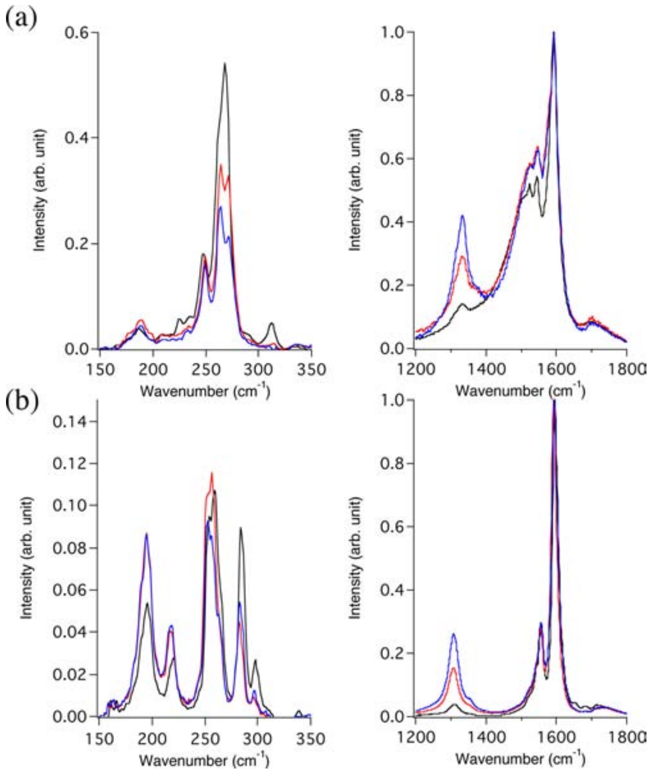


Figure 10. Raman spectra of SWNTs and SWNTs-SiR$_3$ normalized at the G band. SWNTs (black); R = Et (red); and R = Me (blue). Excitation wavelengths: (a) 514.5 nm. (b) 633 nm.

the relative RBM peak intensity of SWNTs-R (R = ^{n}Bu, ^{i}Pr, ^{t}Bu) toward that of SWNTs as a function of SWNT diameter. It is clearly shown that the reductive alkylation of SWNTs took place in not only diameter but also band-structure selectivity. This result is consistent with the results previously reported by Hirsch et al.[36] Spectroscopic analysis of SWNTs-R revealed that the steric hindrance of alkyl groups and the stability of radical intermediates determine the degree of functionalization.

Recently, reductive functionalization of SWNTs with carbonyl compounds was conducted because the functional groups on SWNTs produced from these compounds can be reactive parts for secondary functionalization.[24,25,41,42] The secondary functionalization of SWNTs-R is expected to be a useful reaction for the practical use of SWNTs. Therefore, we studied the reaction of SWNTs with (3-bromopropyloxy)-*tert*-butyldimethylsilane and (3-bromo-2,2-dimethylpropyloxy)-*tert*-butyldimethylsilane. These compounds are useful for reductive alkylation with SWNTs, and a hydroxy group can be used for secondary functionalization after removal of the protecting group, the *tert*-butyldimethylsilyl (TBDMS) group. The reductive alkylation of SWNTs with (3-bromopropyloxy)-*tert*-butyldimethylsilane and (3-bromo-2,2-dimethylpropyloxy)-*tert*-butyldimethylsilane followed by the deprotection reaction using hydrochloric acid gave the SWNTs-$(CH_2)_3OH$ and SWNTs-$CH_2C(CH_3)_2CH_2OH$, respectively. The D/G ratio at the excitation wavelengths of 514.5 and 633 nm of SWNTs-R were determined. (SWNTs-$(CH_2)_3OH$: $D/G_{514.5} = 0.50$, $D/G_{633} = 0.41$; SWNTs-$CH_2C(CH_3)_2CH_2OH$: $D/G_{514.5} = 0.24$, $D/G_{633} = 0.12$). The functionalization degree of SWNTs-$(CH_2)_3OH$ and SWNTs-$CH_2C(CH_3)_2CH_2OH$ are respectively lower than those of SWNTs-^{n}Bu and SWNTs-neopentyl. These results indicate that introduction of the functional groups having the protecting group by the reductive alkylation was achieved successfully and controlled by the bulkiness of the substituents.

The effect of substituents' bulkiness on the efficiency of the reductive silylation of SWNTs via Birch reduction was also studied because introduction of silyl groups reportedly tunes the electronic properties of SWNTs.[12−14] Reactions of SWNTs-Li^+ with trimethylchlorosilane and triethylchlorosilane were conducted (see Scheme 3). The characteristic absorptions in the absorption spectra of SWNTs-$SiMe_3$ and SWNTs-$SiEt_3$ decreased, which indicates that sidewall functionalization occurred (Figure 9). Figure 10 shows Raman spectra of SWNTs-$SiMe_3$ and SWNTs-$SiEt_3$, and the D/G ratios of the functionalized SWNTs as determined from Raman spectroscopy are listed in Table 3. The SWNTs-$SiMe_3$ showed a degree of functionalization higher than those of SWNTs-$SiEt_3$ and SWNTs-^{t}Bu, which indicates that steric hindrance in the chlorosilanes is an important factor for functionalization. The degree of functionalization in the reductive silylation of SWNTs is higher than that in the corresponding reductive alkylation.

■ CONCLUSION

Two-step reductive alkylation of SWNTs introduced two functional groups on the SWNT sidewall. The good relation between [D/G] obtained from the Raman spectra and FGC_{exp} determined from TGA was found in Bu-SWNTs-Bu. The degree of functionalization of ^{1}R-SWNTs-^{2}R having two different substituents was estimated using the relation between [D/G] and FGC. The bulkiness of ^{1}R and ^{2}R strongly affects the degree of functionalization and the ratio of and ^{1}R and ^{2}R on the SWNT sidewall. This substituent effect is useful to control the degree of functionalization and the ratio of different functional groups introduced into the multifunctionalization of SWNTs for practical applications.

In addition, the degrees of functionalization in the reductive alkylation and silylation of SWNTs-Li^+ via Birch reduction were respectively affected by the bulkiness of alkyl halides and silyl chloride. The hydroxyl group was also introduced on the SWNT sidewall using a protecting group. It is noteworthy that the degree of functionalization of SWNTs, which affects their electronic properties, can be tuned simply by the bulkiness of the alkyl groups in the alkyl halides and silyl chlorides.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Raman spectra, absorption spectra, TGA data, and SEM images of functionaliaed SWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

akasaka@tara.tsukuba.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research on Innovation Areas (No. 20108001, "pi-Space"), a Grant-in-Aid for Scientific Research (A)(No. 20245006), Grant-in-Aid for Young Scientists (B)(No. 23750035), Nanotechnology Support Project from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

■ REFERENCES

(1) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603.

(2) Bethune, D. S.; Kiang, C. H.; De Vries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, *363*, 605.

(3) Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen, R.; Itkis, M. E.; Haddon, R. C. *Acc. Chem. Res.* **2002**, *35*, 1105.

(4) Bahr, J. L.; Mickelson, E. T.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *Chem. Commun.* **2001**, 193.

(5) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006**, *106*, 1105.

(6) Ausman, K. D.; Piner, R.; Lourie, O.; Ruoff, R. S.; Korobov, M. *J. Phys. Chem. B* **2000**, *104*, 8911.

(7) Karousis, N.; Tagmatarchis, N.; Tasis, D. *Chem. Rev.* **2010**, *110*, 5366.

(8) Bahr, J. L.; Tour, J. M. *J. Mater. Chem.* **2002**, *12*, 1952.

(9) Balasubramanian, K.; Burghard, M. *Small* **2005**, *1*, 180.

(10) Hirsch, A.; Vostrowsky, O. *Top. Curr. Chem.* **2005**, *245*, 193.

(11) Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4002.

(12) Maeda, Y.; Sato, Y.; Kako, M.; Wakahara, T.; Akasaka, T.; Lu, J.; Nagase, S.; Kobori, Y.; Hasegawa, T.; Motomiya, K.; Tohji, K.; Kasuya, A.; Wang, D.; Yu, D.; Gao, Z.; Han, R.; Ye, H. *Chem. Mater.* **2006**, *18*, 4205.

(13) Kumashiro, R.; Hiroshiba, N.; Komatsu, N.; Akasaka, T.; Maeda, Y.; Suzuki, S.; Achiba, Y.; Hatakeyama, R.; Tanigaki, K. *J. Phys. Chem. Solids* **2008**, *69*, 1206.

(14) Chang, K.; Berber, S.; Tománek, D. *Phys. Rev. Lett.* **2008**, *100*, 236102.

(15) Mickelson, E. T.; Huffman, C. B.; Rinzler, A. G.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *Chem. Phys. Lett.* **1998**, *296*, 188.

(16) Boul, P. J.; Liu, J.; Mickelson, E. T.; Huffman, C. B.; Ericson, L. M.; Chiang, I. W.; Smith, K. A.; Colbert, D. T.; Hauge, R. H.; Margrave, J. L.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, *310*, 367.

(17) Chattopadhyay, J.; Sadana, A. K.; Liang, F.; Beach, J. M.; Xiao, Y.; Hauge, R. H.; Billups, W. E. *Org. Lett.* **2005**, *7*, 4067.
(18) Liang, F.; Sadana, A. K.; Peera, A.; Chattopadhyay, J.; Gu, Z.; Hauge, R. H.; Billups, W. E. *Nano Lett.* **2004**, *4*, 1257.
(19) Chattopadhyay, J.; Chakraborty, S.; Mukherjee, A.; Runtang, W.; Engel, P. S.; Billups, W. E. *J. Phys. Chem. C* **2007**, *111*, 17928.
(20) García-Gallastegui, A.; Obieta, I.; Bustero, I.; Imbuluzqueta, G.; Arbiol, J.; Miranda, J. I.; Aizpurua, J. M. *Chem. Mater.* **2008**, *20*, 4433.
(21) Mukherjee, A.; Combs, R.; Chattopadhyay, J.; Abmayr, D. W.; Engel, P. S.; Billups, W. E. *Chem. Mater.* **2008**, *20*, 7339.
(22) Syrgiannis, Z.; Hauke, F.; Röhrl, J.; Hundhausen, M.; Graupner, R.; Elemes, Y.; Hirsch, A. *Eur. J. Org. Chem.* **2008**, 2544.
(23) Gebhardt, B.; Graupner, R.; Hauke, F.; Hirsch, A. *Eur. J. Org. Chem.* **2010**, 1494.
(24) Gebhardt, B.; Hoffman, F.; Backes, C.; Müller, M.; Plocke, T.; Maultzsch, J.; Thomsen, C.; Hauke, F.; Hirsch, A. *J. Am. Chem. Soc.* **2011**, *133*, 19459.
(25) Gebhardt, B.; Syrgiannis, Z.; Backes, C.; Graupner, R.; Hauke, F.; Hirsch, A. *J. Am. Chem. Soc.* **2011**, *133*, 7985.
(26) Roubeau, O.; Lucas, A.; Pénicaud, A.; Derré, A. *J. Nanosci. Nanotechnol.* **2007**, *7*, 3509.
(27) Maeda, Y.; Kato, T.; Hasegawa, T.; Kako, M.; Akasaka, T.; Lu, J.; Nagase, S. *Org. Lett.* **2010**, *12*, 996.
(28) Chen, J.; Chen, S.; Zhao, X.; Kuznetsova, L. V.; Wong, S. S.; Ojima, I. *J. Am. Chem. Soc.* **2008**, *130*, 16778.
(29) Stephenson, J. J.; Hudson, J. L.; Leonard, A. D.; Prince, K. B.; Tour, J. M. *Chem. Mater.* **2007**, *19*, 3491.
(30) Brunetti, F. G.; Herrero, M. A.; Muñoz, J. D. M.; Díaz-Ortiz, A.; Alfonsi, J.; Meneghetti, M.; Prato, M.; Vázquez, E. *J. Am. Chem. Soc.* **2008**, *130*, 8094.
(31) Ménard-Moyon, C.; Fabbro, C.; Prato, M.; Bianco, A. *Chem.—Eur. J.* **2011**, *17*, 3222.
(32) Heister, E.; Neves, V.; Tilmacu, C.; Lipert, K.; Beltrán, V. S.; Coley, H. M.; Silva, S. R. P.; McFadden, J. *Carbon* **2009**, *47*, 2152.
(33) Hu, H.; Zhao, B.; Hamon, M. A.; Kamaras, K.; Itkis, M. E.; Haddon, R. C. *J. Am. Chem. Soc.* **2003**, *125*, 14893.
(34) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95.
(35) Maeda, Y.; Kimura, S. I.; Hiroshima, Y.; Kanda, M.; Lian, Y.; Wakahara, T.; Akasaka, T.; Hasegawa, T.; Tokumoto, H.; Shimizu, T.; Kataura, H.; Miyauchi, Y.; Maruyama, S.; Kobayashi, K.; Nagase, S. *J. Phys. Chem. B* **2004**, *108*, 18395.
(36) Wunderlich, D.; Hauke, F.; Hirsch, A. *J. Mater. Chem.* **2008**, *18*, 1493.
(37) Saito, T.; Ohmori, S.; Shukla, B.; Yumura, M.; Lijima, S. *Appl. Phys. Exp.* **2009**, *2*, 095006.
(38) Bachilo, S. M.; Strano, M. S.; Kittrell, C.; Hauge, R. H.; Smalley, R. E.; Weisman, R. B. *Science* **2002**, *298*, 2361.
(39) Kukovecz, A.; Kramberger, C.; Georgakilas, V.; Prato, M.; Kuzmany, H. *Eur. Phys. J. B* **2002**, *28*, 223.
(40) Moore, V. C.; Strano, M. S.; Haroz, E. H.; Hauge, R. H.; Smalley, R. E.; Schmidt, J.; Talmon, Y. *Nano Lett.* **2003**, *3*, 1379.
(41) Chattopadhyay, J.; De Jesus Cortez, F.; Chakraborty, S.; Slater, N. K. H.; Billups, W. E. *Chem. Mater.* **2006**, *18*, 5864.
(42) Moniruzzaman, M.; Chattopadhyay, J.; Billups, W. E.; Winey, K. I. *Nano Lett.* **2007**, *7*, 1178.