Synthesis of, Light Emission from, and Optical Power Limiting in Soluble Single-Walled Carbon Nanotubes Functionalized by Disubstituted Polyacetylenes

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Single-walled carbon nanotubes are covalently functionalized by conjugated polyacetylenes through their cyclization reactions with poly(1-phenyl-1-alkyne) (**3**) and poly(diphenylacetylene) derivatives (**6**) carrying azido functional groups at the ends of their alkyl pendants. The resultant polyene nanotube addends (**7** and **8**) are soluble in common solvents, emit intense visible lights and strongly attenuate the power of harsh laser pulses.
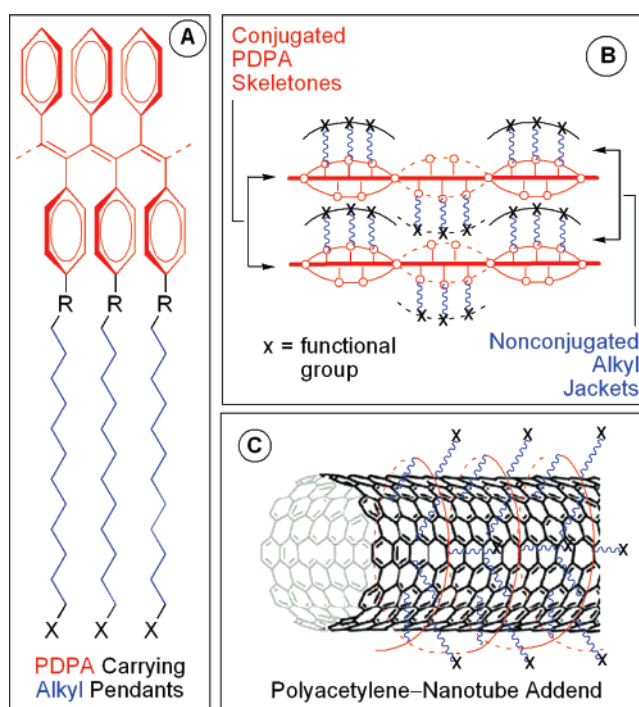
Introduction

Carbon nanotubes possess an array of outstanding materials properties.[1] Their notorious insolubility and intractability have, however, significantly limited the scope of their practical applications. Many research groups have taken various approaches toward enhancing the processability of the nanotubes.[2,3] In 1999, we developed a "polymer-wrapping" process—we used soluble poly(phenylacetylene) chains to wrap the multiwalled carbon nanotubes, which rendered the nanotubes soluble in common organic solvents.[4,5] We revealed that the polyacetylene nanotube composites strongly attenuated the harsh laser pulses, thanks to the optical nonlinearity of the carbon nanotubes. On the other hand, we found that the luminescence of poly(phenylacetylene)[6] was quenched by the nanotubes, due to efficient energy transfer from the polyene chains to the nanotube walls.[4,7]

We are interested in making the nanotubes emissive through molecular functionalization. Conferring luminescent properties on the nanotubes will pave the way to a number of attractive possibilities. The luminescent nanotubes, for example, may work as fluorescent nanosensors and biological probes that will enable direct observation of the nanotubes inside nanostructured devices and living cells using optical microscopes.[8] In this work, we tried to endow single-walled carbon nanotubes (SWNTs) with light-emitting capability, while keeping them nonlinear optically active.

In our previous work, the direct contact of the conjugated poly(phenylacetylene) chains with the carbon nanotube sidewalls facilitated efficient energy transfer, resulting in the undesired luminescence quenching.[4] During the course of our work on the development of highly luminescent polyacetylenes, we have noted that some disubstituted polyacetylenes with long alkyl pendants, e.g., poly(1-phenyl-1-alkyne)s (PPAs; $-\{(C_6H_5)C=C[(CH_2)_mR]\}_n-$), emit blue light very efficiently, with their
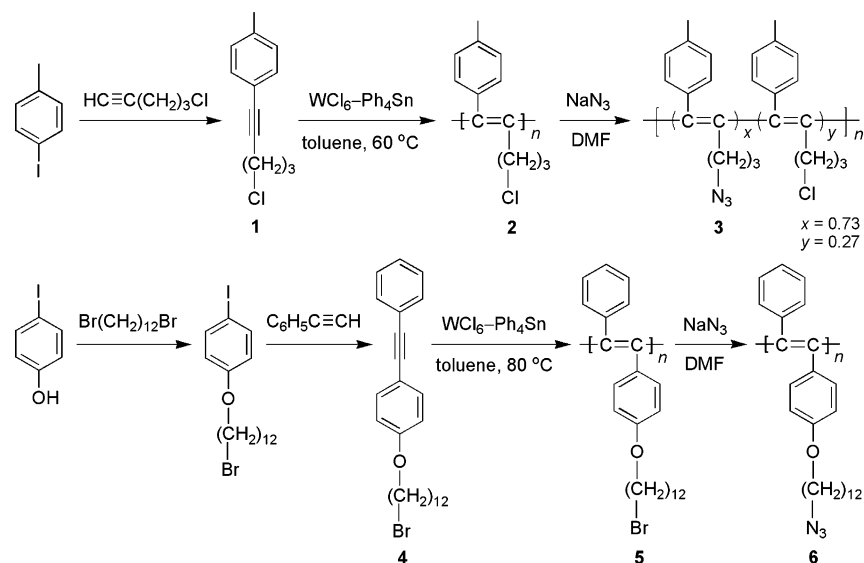
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CHART 1

fluorescence quantum yields (Φ_F) reaching almost unity.[9,10] Some poly(diphenylacetylene) (PDPA) derivatives carrying alkyl chains (Chart 1A) are also highly luminescent (Φ_F up to 98%).[10,11] Furthermore, these polymers do not suffer from the problem of luminescence quenching by aggregate formation[10,12] and remain highly emissive in the solid state.[10] We have attributed this to the "jacket effect" of the alkyl chains.[10,13] To avoid steric crowdedness, the bulky pendant groups of the disubstituted polyacetylenes may helically rotate around their polyene backbones,[10] like in the case of well-known poly(9-vinylcarbazole).[14] The nonconjugated alkyl sheaths keep the conjugated polyene skeletons apart (Chart 1B), which weakens the $\pi-\pi$ interaction of the emitting centers and hampers the formation of excimers, exciplexes, and other detrimental species.

Functional Polyacetylene Carbon Nanotube Addends

J. Phys. Chem. B, Vol. 110, No. 5, 2006 **2303**

SCHEME 1

Taking the jacket effect of the alkyl pendant groups into consideration, in this work, we designed and synthesized two substituted polyacetylenes carrying functional groups (X) at the ends of their alkyl chains. The X group we used is azido (N_3), which is known to undergo cycloaddition reactions with the strained double bonds in fullerenes and nanotubes.[15,16] It is hoped that, after the polymer chains are attached to the SWNT walls, the alkyl spacers will serve as buffer layers to prevent direct contact of the polymer chains with the nanotube walls (Chart 1C), hence impeding the energy transfer from the former to the latter. In this paper, we prove that this design strategy works. We further show that our approach has enabled us to combine the advantageous attributes of the components in the hybrid products: the resultant polyacetylene nanotube addends are both light-emitting and optical-limiting.

Experimental Section

Materials. Toluene (BDH) and THF (Labscan) were distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use. Triethylamine (RdH) was distilled over potassium hydroxide. SWNTs were purchased from MER (Tucson, AZ) and further purified in our laboratories according to published procedures.[1y] Copper(I) iodide, sodium azide, phenylacetylene, 5-chloro-1-pentyne, triphenylphosphine, dichlorobis(triphenylphosphine)palladium(II), 4-iodotoluene, 4-iodophenol, 1,12-dibromododecane, 1,2-dichlorobenzene, and other reagents and solvents used in this study were all purchased from Aldrich and used as received without further purification.

Instrumentation. ^1H and ^{13}C NMR spectra were measured on a Bruker ARX 300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. Fourier transform infrared spectra were taken on a Perkin-Elmer 16 PC spectrometer. UV−vis absorption spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectra were taken on a SLM 8000C spectrofluorometer. The Φ_F values were determined using 9,10-diphenylanthracene in cyclohexane ($\Phi_F = 90\%$) as standard. Thermal analysis was carried out on a Setaram thermogravimetric analyzer TGA 92 at a heating rate of 20 °C/min under nitrogen. Molecular weights and polydispersity indexes of the polymers were estimated by a Waters 510 gel permeation chromatography (GPC) system equipped with RI and UV detectors, with the

working wavelength of the UV detector set at 254 nm, using a set of monodisperse polystyrenes as calibration standards and THF as eluent at a flow rate of 1.0 mL/min. Elemental microanalyses were performed by M−H−W Laboratories (Phoenix, AZ). Electron micrographs were taken on a JEOL 2010 transmission electron microscope operating at an accelerating voltage of 200 kV.

Optical limiting experiments were carried out at 532 nm, using 8-ns optical pulses generated from a frequency-doubled Q-switched Nd:YAG laser (Quanta Ray GCR-3) operating in a near-Gaussion transverse mode with a repetition rate of 10 Hz. The pulsed laser beam was focused onto a 1-cm square quart cell filled with a THF solution of the SWNT addend. The incident and transmitted energies were measured by an OPHIR detector (30-A-Diff-SH), and every point of the optical limiting data was the average of at least 15 laser shots. The detector was connected to a computer before and after the optical limiting data were taken, and the output stability of the laser equipment was doubled checked by taking a series of output data by the energy meter every 10 s for an extended period of time.

PL lifetime measurements were conducted using laser pulses of 267 nm as excitation wavelength, which was produced by the frequency summation of 800 nm with its 400-nm frequency doubling from a Ti:sapphire regenerative amplifier (200-fs pulse width and 1 kHz repetition rate). For time-resolved PL measurements, the PL signals near the emission peaks were collimated and focused onto the entrance slit of a monochromator with the output plane connected to a synchroscan streak camera (Hamamatsu C4334, 20 ps resolution). In the optical setup, a flip mirror was inserted before the monochromator-streak camera system in order to reflect the PL to a fiber spectrometer (Ocean Optics Inc.) to record the time-integrated PL spectra before each run of lifetime measurement. The laser energy level for excitation was ∼400 μW.

Syntheses. The disubstituted acetylene monomers (**1** and **4**) and their polymers (**2**, **3**, **5**, and **6**) were prepared according to the synthetic routes shown in Scheme 1.

1-(4-Tolyl)-5-chloro-1-pentyne (1). To a 250-mL flask were added 30 mg copper(I) iodide, 110 mg dichlorobis(triphenylphosphine)palladium, and 30 mg triphenylphosphine in a glovebox. Triethylamine (150 mL), 4-iodotoluene (3.27 g, 15 mmol), and 5-chloro-1-pentyne (1.53 g, 15 mmol) were then injected. The resultant mixture was stirred at room temperature

overnight. The solid was removed by filtration, and the solvent was evaporated by a rotary evaporator. The crude product was purified on a silica gel column using chloroform as eluent. Colorless oil of **1** was obtained in 69% yield (1.98 g). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.32 (d, 2H), 7.13 (m, 2H), 3.74 (t, 2H), 2.62 (t, 2H), 2.36 (s, 3H), 2.06 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 138.3, 132.0, 129.4, 121.1, 87.8, 82.1, 44.3, 32.1, 21.8, 17.2.

Poly[1-(4-tolyl)-5-chloro-1-pentyne] (2). Into a baked 20-mL Schlenk tube with a stopcock in the sidearm was added 0.50 g of **1**. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the sidearm. Freshly distilled toluene (6 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 47.7 mg of tungsten(VI) chloride and 51.6 mg of tetraphenyltin in 6 mL of toluene. The two tubes were aged at 60 °C for 15 min, and the monomer solution was transferred to the catalyst solution using a hypodermic syringe. The reaction mixture was stirred at 60 °C for 24 h. The solution was then cooled to room temperature, diluted with 15 mL of chloroform, and added dropwise to 1500 mL of methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight and was then filtered. The polymer was washed with methanol and dried in a vacuum oven to a constant weight (0.44 g, 88%). $M_w = 20\,400$, $M_w/M_n = 2.58$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 818 (C–Cl stretch). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.12–5.37 (Ar–H), 3.98–2.70 (–CH$_2$Cl), 2.69–1.78 (Ar–C*H*$_3$, CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 143.8–134.2, 131.3–124.9, 47.8–43.6, 36.0–28.4, 22.7–20.7.

Poly{[1-(4-tolyl)-5-chloro-1-pentyne]-co-[1-(4-tolyl)-5-azido-1-pentyne]} (3). Into a 20-mL Schlenk tube were added 0.24 g of **2** (1.25 mmol), 0.3 g of NaN$_3$ (4.6 mmol), and 3 mL of DMF. The mixture was stirred at 60 °C for 40 h and was then poured into 40 mL of water at 0 °C. The precipitate was collected by filtration. The solid was dissolved in THF, and the insoluble residue was filtered out. The filtrate was added dropwise to 500 mL of methanol under stirring. The precipitate was allowed to stand overnight, which was then filtered and dried to a constant weight (0.21 g, 87%). $M_w = 19\,400$, $M_w/M_n = 2.76$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 2095 (–N$_3$ stretch), 818 (C–Cl stretch). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.12–5.22 (Ar–H), 3.64–2.67 (–CH$_2$Cl, –CH$_2$N$_3$), 2.65–1.84 (Ar–C*H*$_3$, CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 144.7–134.6, 131.5–125.6, 53.7–50.9, 47.2–43.6, 35.8–24.4, 22.9–20.5. UV (THF, 0.007 mg/mL): λ_{max} (nm): 239, ~325 (shoulder). Found: C, 71.60; H, 5.89; N, 15.54.

1-Phenyl-2-[4-(12-bromododecyloxy)phenyl]acetylene (4). To a 500-mL round-bottomed flask were added 4.3 g of 4-iodo-phenol (19.3 mmol), 6.4 g of 1,12-dibromo-dodecane (19.4 mmol), 1.1 g of potassium hydroxide (19.6 mmol), 0.3 g of potassium iodide, and 200 mL of acetone/DMSO (10:1). The mixture was refluxed for 24 h. The solid was removed by filtration, and the solvent was evaporated. The crude product was purified on a silica gel column using chloroform/hexane (1:2) as eluent. White solid of 1-(12-bromododecyloxy)-4-iodobenzene was obtained in 40% yield (3.6 g). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.52 (d, 2H), 6.67 (d, 2H), 3.91 (t, 2H), 3.42 (t, 2H), 1.85 (m, 2H), 1.77 (m, 2H), 1.27 (m, 16H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 159.0, 138.4, 117.1, 82.4, 68.3, 34.2, 33.5, 33.2, 31.0, 29.9, 28.8, 28.3, 26.1.

To a 250-mL flask were added 15 mg of copper(I) iodide, 50 mg of dichlorobis(triphenylphosphine)-palladium, 15 mg of

SCHEME 2
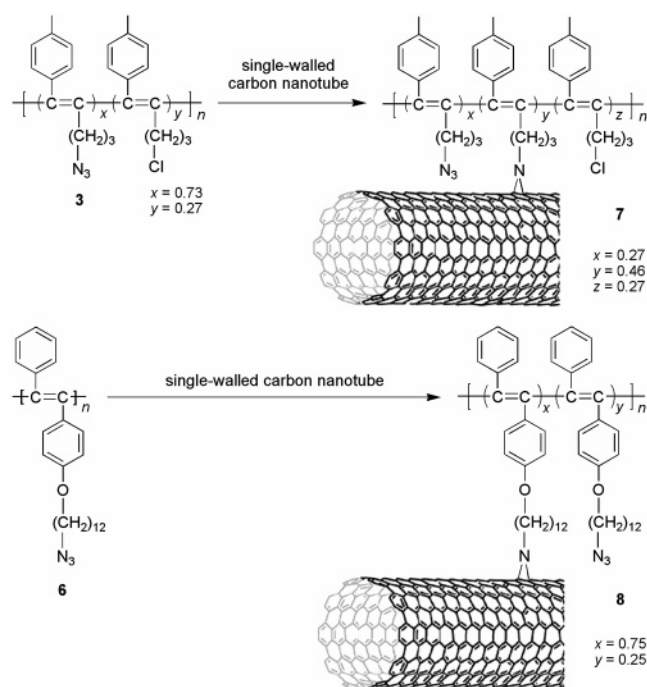
triphenylphosphine, and 3.6 g of 1-(12-bromododecyloxy)-4-iodobenzene (7.7 mmol) in a glovebox. Triethylamine (150 mL) and phenylacetylene (1.0 g, 9.8 mmol) were then injected. The resultant mixture was stirred at room temperature overnight. The solid was removed by filtration, and the solvent was evaporated. The crude product was purified on a silica gel column using chloroform as eluent. Colorless stick oil of **3** was obtained in 45.6% yield (1.99 g). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.45 (m, 4H), 7.33 (m, 3H), 6.82 (d, 2H), 3.92 (t, 2H), 3.37 (t, 2H), 1.80 (m, 4H), 1.27 (m, 16H).

Poly{1-phenyl-2-[4-(12-bromododecyloxy)phenyl]acetyl-ene} (5). This polymer was synthesized by a procedure similar to that described above for the preparation of **2**. The polymer was obtained in 53% yield. $M_w = 13\,600$, $M_w/M_n = 1.55$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 552 (C–Br stretch). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.13–6.42 (Ar–H), 6.30–5.86 (Ar–H), 4.01–3.59 (–OCH$_2$), 3.48–3.33 (–CH$_2$Br), 1.97–1.03 (CH$_2$).

Poly{1-phenyl-2-[4-(12-azidododecyloxy)phenyl]acetylene} (6). This polymer was synthesized by a procedure similar to that described above for the preparation of **3**. The polymer was obtained in 83% yield. $M_w = 17\,300$, $M_w/M_n = 1.42$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 2095 (–N$_3$ stretch). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.14–6.41 (Ar–H), 6.30–5.90 (Ar–H), 4.02–3.58 (–OCH$_2$), 3.34–3.17 (–CH$_2$N$_3$), 1.90–1.13 (CH$_2$). UV (THF, 0.007 mg/mL): λ_{max} (nm): 238, 366, 427. Found: C, 78.09; H, 8.04; N, 10.05.

Nanotube Functionalization. The polyacetylene-SWNT addends (**7** and **8**) were prepared via the synthetic routes given in Scheme 2.

Poly{[1-(4-tolyl)-5-chloro-1-pentyne]-co-[1-(4-tolyl)-5-azido-1-pentyne]}–SWN T Addend (7). Into a baked 150-mL Schlenk tube with a stopcock in the sidearm were added SWNT (30 mg), **3** (55 mg), and 1,2-dichlorobenzene (25 mL). The tube was evacuated under vacuum and then flushed with nitrogen six times through the sidearm. After stirring 15 h at room temperature, the black suspension was heated to, and stirred at, 110 °C under nitrogen for 70 h. After cooling to room temperature, the insoluble dark solid was filtered out and washed

Functional Polyacetylene Carbon Nanotube Addends

J. Phys. Chem. B, Vol. 110, No. 5, 2006 **2305**

TABLE 1: Polymerization Results and Characterization Data

	yield (%)	M_w^a	M_w/M_n^a	λ_{max}^b (nm)	Φ_F^c (%)	molar fraction^d		lifetime (ns)^d	
polymer						A_1	A_2	τ_1	τ_2
2	88	20 400	2.58	467	10	0.41	0.59	0.13	1.01
3	87	19 400	2.76	467	10	0.34	0.66	0.17	1.11
7^e	76	20 600	3.30	468	9	0.38	0.62	0.17	1.37
5	53	13 600	1.55	505	22		1.00		1.42
6	83	17 300	1.42	505	23		1.00		1.08
8^e	86	23 400	1.68	505	19		1.00		1.23

^{a} Determined by GPC in THF on the basis of a polystyrene calibration. ^{b} Maximum wavelength of light emission from THF solution. ^{c} Fluorescence quantum yield in THF using 9,10-diphenyl-anthracene in cyclohexane ($\Phi_F = 90\%$) as standard. ^{d} Fluorescence decay. ^{e} Weight contents of SWNT in the two polymers determined by TGA[4] are 16.4 and 18.8% for **7** and **8**, respectively.

with THF. The solvent in the filtrate was removed to yield deep dark product, which was air dried. The product was dissolved in THF and the resultant solution was allowed to stand for several days and was then filtered by a cotton filter to remove insoluble particles, if any. (Actually there were no observable insoluble particles and the solution was always clear during the standing period.) The product was further purified by eluting it through a silica gel column using THF/DMF (4:1) as eluent. The solvent was removed and the final product was dried under vacuum at 40 °C to a constant weight (50 mg, 76%). $M_w = 20\,600$, $M_w/M_n = 3.30$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 2095 ($-N_3$ stretch), 817 (C$-$Cl stretch). UV (THF, 0.007 mg/mL): λ_{max} (nm): 239, $\sim$340 (shoulder).

Poly{1-phenyl-2-[4-(12-azidododecyloxy)phenyl]acetylene}$-$SWNT Addend (8). This addend was synthesized by a procedure similar to that for the preparation of **7**, using 15 mg of SWNT and 48 mg of **6** as starting materials. The addend was obtained in 86% yield (51 mg). $M_w = 23\,400$, $M_w/M_n = 1.68$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 2095 ($-N_3$ stretching). UV (THF, 0.007 mg/mL): λ_{max} (nm) 238, 366, 427.

Results and Discussion

Polymer Syntheses. PPA and PDPA are highly luminescent polyacetylenes.[10] To molecularly meld them with SWNTs, it is necessary to make them reactive to the nanotubes. Azido group is known to react with SWNTs,[16] but direct polymerizations of 1-phenyl-1-alkyne and diphenylacetylene monomers containing azido moieties are prevented by the "poisoning effect" of the azido group on the transition-metal catalysts. We designed two 1-phenyl-1-alkyne and diphenylacetylene precursors carrying chloro (**1**) and bromo groups (**4**), which can later be readily transformed to azido group by postpolymerization reactions (cf., Scheme 1). The halogen groups are less "toxic" and are expected to be polymerized by the common metathesis catalysts such as WCl$_6$$-Ph_4$Sn.

The synthetic results are summarized in Table 1. The end-chlorinated 1-phenyl-1-pentyne monomer (**1**) is polymerized by WCl$_6$$-Ph_4$Sn in toluene at 60 °C into a polymer with a high molecular weight ($>20 \times 10^3$) in an excellent yield (88%). The resultant polymer (**2**) is subject to a reaction with sodium azide, which converted 73% of the chloro groups to the azido groups, resulting in the formation of copolymer **3**. Similarly, the end-brominated diphenylacetylene monomer (**4**) is readily polymerized. The bromo groups of the precursor polymer (**5**) are completely replaced by the azido groups, probably due to the higher reactivity of the bromide with the azide.

TABLE 2: Synthesis of PPA SWNT Addends (7)^a

no.	SWNT (mg)	**3** (mg)	DCB (mL)	temp (°C)	time (h)	solubility	azido residue
1	30	119	30	150	70	insoluble	no
2	19	37	20	b	b	insoluble	no
3	30	55	25	110	70	soluble	yes
4	10	50	20	110	90	soluble	yes

^{a} Carried out in 1,2-dichlorobenzene (DCB) under nitrogen. The reaction mixture was first stirred at room temperature for 10 h and then heated to the desired temperature for the specified period of time. ^{b} The reaction mixture was stirred at 110 °C for 63 h and then 130 °C for 56 h.
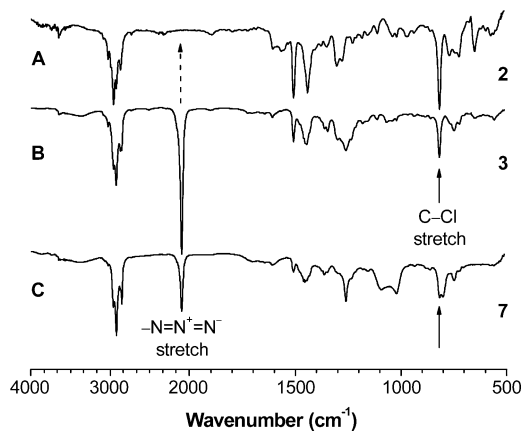
Figure 1. IR spectra of (A) **2**, (B) **3**, and (C) **7**.

Polymer SWNT Hybridization. Heating a mixture of **3** and SWNT in dichlorobenzene at 150 °C for 70 h gives a product containing no azido group, but the purified PPA SWNT addend is unfortunately insoluble (Table 2, no. 1). Similar result is obtained when the cycloaddition reaction is conducted at 130 °C. Lowering the reaction temperature to 110 °C helps: deep dark solutions are resulted after the reaction mixtures are stirred at the "low" temperature for about 3 days. The PPA SWNT addends (**7**) remain soluble after isolation and purification, although the products contain some unreacted azido moieties (Table 2, nos. 3 and 4). To exclude the possibility that the polymers are physically absorbed onto the SWNTs, the purified products are passed through a silica gel column using THF/DMF (4:1) as eluent, in which the SWNTs are insoluble. Nothing is left in the column, and the silica gel particles maintain as white as newly packed into the column, confirming that PPA and SWNT are covalently bound together.

The PPA SWNT addends possess high molecular weights with somewhat broadened polydispersity indexes, as can be seen from the example given in Table 1. The SWNT content in **7** is estimated by TGA pyrolysis at 1100 °C[4,16a] to be $\sim$16 wt %. Similarly, the PDPA SWNT addend (**8**) is prepared, whose molecular weight and SWNT content are both higher than those of its PPA SWNT counterpart (**7**).

Structural Characterization. The excellent solubility of the polymers in common organic solvents enables their molecular structures to be characterized by various spectroscopic methods, from which satisfactory analysis data are obtained (see Experimental Section for details). Figure 1 shows a set of examples of the IR spectra for poly[1-(4-tolyl)-5-chloro-1-pentyne] (**2**), poly{[1-(4-tolyl)-5-chloro-1-pentyne]-co-[1-(4-tolyl)-5-azido-1-pentyne]} (**3**), and PPA SWNT addend **7**. Polymer **2** exhibits no absorption band at $\sim$2000 cm^{-1} but a strong C$-$Cl band at 818 cm^{-1}.[17] Its reaction product with sodium azide, i.e., polymer **3**, absorbs strongly at 2093 cm^{-1} due to azido stretching,[17] with the intensity of C$-$Cl band at 818 cm^{-1} decreased (Figure 1B).
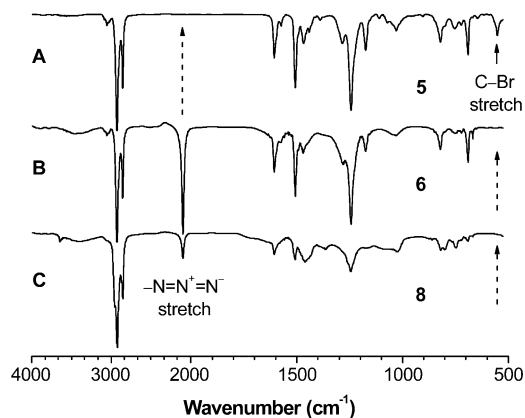
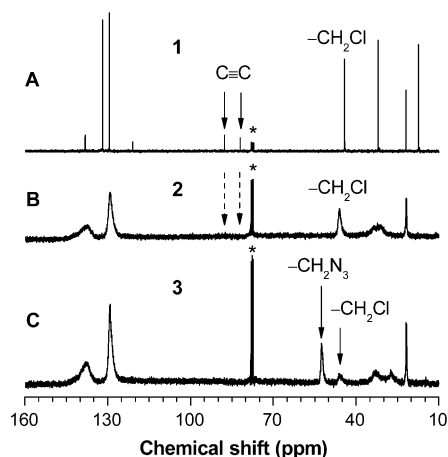**Figure 2.** IR spectra of (A) **5**, (B) **6**, and (C) **8**.

Figure 3. ^{13}C NMR spectra of (A) **1**, (B) **2**, and (C) **3** in chloroform-*d*. The solvent peaks are marked with asterisks.

The PPA SWNT addend (**7**) gives a weaker azido stretching band, indicting that part of the azido groups of **3** has reacted with SWNTs. The amount of the unreacted azido groups is calculated using the relative intensities of the absorption peaks at 2093 (azido band) and 2929 cm^{-1} (reference band), from which the molar composition of the PPA-SWNT addend (**7**) is estimated (cf., Scheme 2). Poly{1-phenyl-2-[4-(12-bromo-dodecyloxy)phenyl]acetylene} (**5**), poly{1-phenyl-2-[4-(12-azido-dodecyloxy)phenyl]acetylene} (**6**), and PDPA SWNT addend **8** exhibit similar spectral features[17] (Figure 2), from which the molecular structures of the polymers are confirmed and the molar composition of the addend is estimated.

Figure 3 shows the ^{13}C NMR spectra of monomer **1** and polymers **2** and **3**. The acetylenic carbon atoms of monomer **1** resonate at δ 87.8 and 82.1, while the resonance of its carbon atom linked to the chlorine atom occurs at about δ 45. In the spectrum of its polymer (**2**), the acetylenic resonance peaks are completely absent, which duly confirms the occurrence of the expected acetylene polymerization (Figure 3B). After **2** reacts with sodium azide, the intensity of the peak at δ 46.3 decreases, with a new peak at δ 52.6 appearing (Figure 3C). This new peak is readily assignable to $-CH_2N_3$ resonance,[17] thus verifying the partial substitution of the chlorine atoms by the azido groups.

The resonance peak of the protons of the methylene group linked to the bromine atom at δ 3.42 in the spectrum of polymer **5** (Figure 4A) completely disappears in the spectrum of polymer **6**, while a new resonance peak appears at δ 3.25, which is attributed to the resonance of the protons of the methylene unit linked to the azido functional group (Figure 4B).[17] This duly substantiates the finding by the IR analysis of the polymers (cf.,
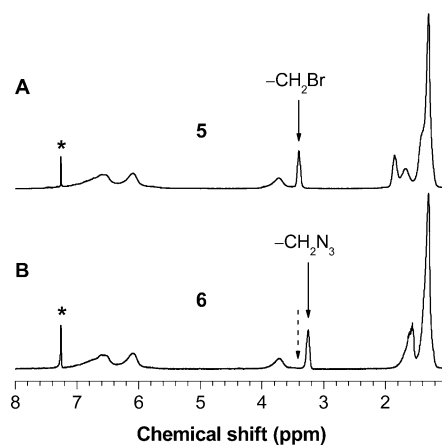

Figure 4. ^{1}H NMR spectra of (A) **5** and (B) **6** in chloroform-*d*. The solvent peaks are marked with asterisks.
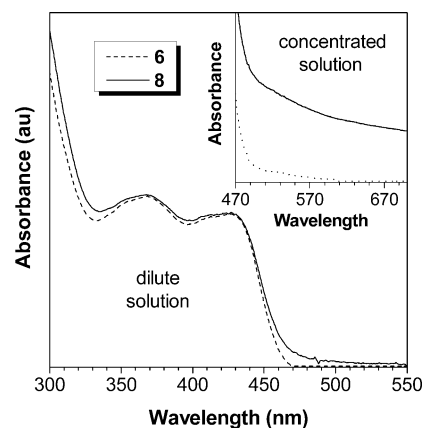

Figure 5. UV$-$vis absorption spectra of dilute (7×10^{-3} mg/mL) and concentrated solutions (70×10^{-3} mg/mL; inset) of **6** and **8** in THF.

Figure 2): the bromo groups in **5** have been completely consumed by the substitution reaction with sodium azide to yield the azido-functionalized polymer **6** (cf., Scheme 1).

Figure 5 shows the UV$-$vis spectra of the THF solutions of polymer **6** and its SWNT addend **8**. The dilute solution of **8** gives a spectrum almost identical to that of its precursor **6**, except for the long tail in the visible region due to the nanotube absorption.[2k,4,7,16b] While the dilute solution is transparent due to its weak nanotube absorption, the solutions with higher concentrations are deeply dark colored. This is evidenced by the spectrum of a concentrated solution of **8** shown in the inset of Figure 5; the nanotube absorption is now strong and covers the entire visible spectral region.

To further confirm the presence of the SWNTs in the polymers, the addends are analyzed by electron microscopes. A set of examples of the transmission electron microscopy (TEM) micrographs of PPA SWNT addend **7** is shown in Figure 6. The nanotubes are clearly seen. The high-magnification micrographs reveal that the amorphous polymer chains are wrapping around the nanotube walls.

Optical Properties. All the polymers and addends are soluble in common organic solvents. The dilute solutions of addends **7** and **8** are deeper colored than those of their precursor polymers **3** and **6** but are still optically transparent, as evidenced by the clear observation of putting pencils behind the vials (Figure 7). This optical transparency allows one to visually verify the nonexistence of insoluble particles suspending in the solutions. The polymers and addends are luminescent: under illumination of a handheld UV lamp, the PPA and PDPA SWNT addends **7**
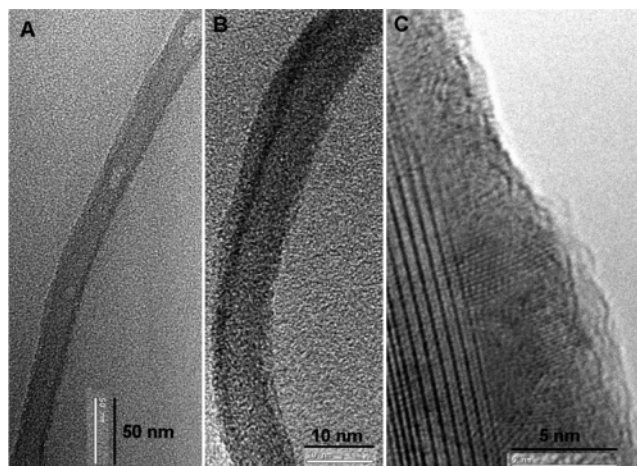
Functional Polyacetylene Carbon Nanotube Addends

J. Phys. Chem. B, Vol. 110, No. 5, 2006 **2307**

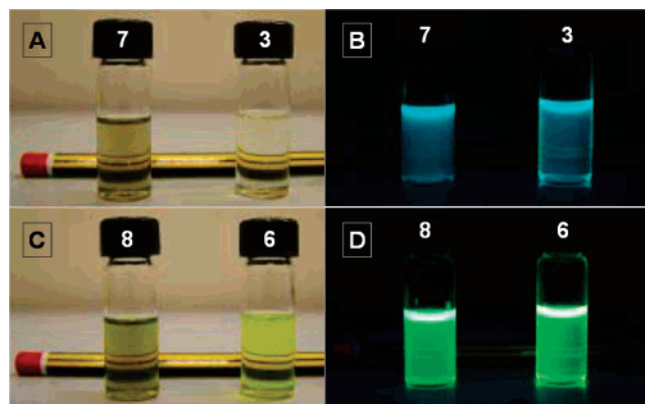**Figure 6.** TEM microphotographs of **7**.

Figure 7. Photographs of THF solutions of polyacetylene SWNT addends **7** and **8** taken under (A and C) normal laboratory lighting and (B and D) UV illumination. Photographs of THF solutions of their precursor polymers **3** and **6** are shown for comparison.
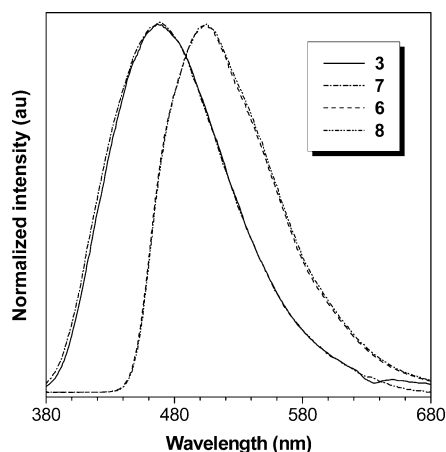

Figure 8. PL spectra of THF solutions of **3** and **6**−**8**. Solution concentration (mg/mL), 0.007 (**3**, **6**, and **7**) and 0.008 (**8**); excitation wavelengths (nm), 360 (**3**), 346 (**7**), and 371 (**6** and **8**).

and **8**, respectively, emit blue and green lights, as do their precursor polymers **3** and **6**.[10]

Figure 8 shows the emission spectra of THF solutions of the addends; the spectra of their precursor polymers are given in the same figure for comparison. The PL spectrum of addend **7** virtually overlaps with that of its precursor **3**, with their λ_{max} and Φ_F values being almost identical (Table 1). Furthermore, their PL decay curves are similar (Figure 9A), with little changes observed in their dynamic parameters A and τ (Table 1). In our
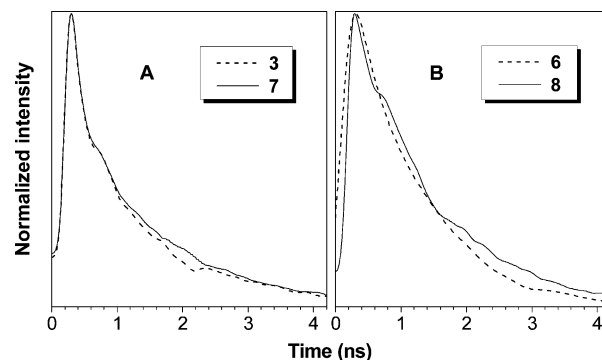

Figure 9. Fluorescence decay curves of THF solutions of (A) **3** and **7** and (B) **6** and **8**. Excitation wavelength: 267 nm.
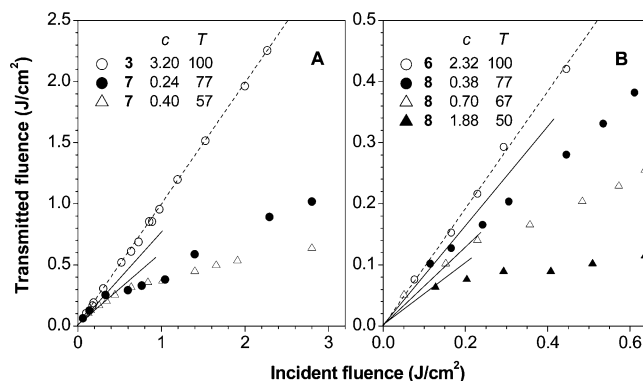

Figure 10. Optical-limiting response of THF solutions of polyacetylene SWNT addends (A) **7** and (B) **8** to 8-ns, 10-Hz pulses of 532-nm laser light. Light transmission curves of THF solutions of precursor polymers **3** and **6** are shown for comparison. Abbreviations: c = solution concentration (mg/mL), T = linear transmittance (%).

previous work, the nanotubes has quenched the PL of poly-(phenylacetylene), a conjugated polyene with no alkyl pendants.[4] The SWNTs are not quenching the luminescence of **3**, a poly-(phenylacetylene) derivative carrying nonconjugated alkyl pendants, thanks to the jacket effect of the alkyl spacers. The emission spectra and decay curves of polymer **7** and its addend **8** are also similar, again with little changes observed in their emission efficiencies and dynamics. The Φ_F values of **6** and **8** are, respectively, more than 2-fold higher than those of **3** and **6** (Table 1), in agreement with our early finding that a polyacetylene carrying longer alkyl pendants emits more efficiently than its congener bearing shorter alkyl pendants.[10]

The optical power limiting behaviors of the polymer SWNT addends are investigated, employing the experimental setup used in our previous studies on the nonlinear optical properties of polymer-fullerene addends[18] and hyperbranched polyarylenes.[19] When the THF solution of polymer **3** is shot by 8-ns pulses of 532-nm laser light, the transmitted fluence linearly increases with an increase in the input fluence (Figure 10A). This polymer, like other polyacetylenes, is thus nonlinear optically inactive. The solutions of its SWNT addend **7**, however, respond to the optical pulses in a different way. The linear transmittance (T) of a dilute solution of **7** with a concentration of 0.24 mg/mL is 77%, lower than that of the solution of its precursor polymer **3**, although the concentration of **7** is less than one tenth of that of the solution of **3**. As the incident fluence is increased, the solution of **7** becomes more opaque. The optical power-limiting effect of the addend solution becomes more pronounced when its concentration is increased to 0.4 mg/mL. At an incident fluence of 2.8 J/cm^2, the transmitted fluence is 0.63 J/cm^2, giving an excellent signal suppression ratio[20] of 0.23. Similarly,

2308 *J. Phys. Chem. B, Vol. 110, No. 5, 2006*

Li et al.

polymer **6** cannot limit the optical power of the laser pulses, but its SWNT addend **8** can (Figure 10B), once again confirming that the optical nonlinearity is originated from the nanotubes. The solution of **8** with a linear transmittance of 50% works as an outstanding optical limiter, offering an impressive signal suppression ratio of 0.18.

In summary, in this study, we have designed and synthesized disubstituted polyacetylenes **2** and **5** carrying halogen atoms at the ends of their alkyl pendants. The chloro and bromo groups are partially and completely replaced through polymer reactions, yielding the azido-functionalized polymers **3** and **6**, respectively. By ulitization of the cyclization reaction of the azido group with the strained double bonds, the polyacetylene chains are attached to the SWNT sidewalls. Our molecular functionalization approach enables the combination of the advantageous properties of the two components in one hybrid system: the polymer makes the addend light emitting, while the nanotube renders it optical limiting. The jacket effect of the alkyl pendants may allow one to introduce other useful functional properties such as liquid crystallinity[10,21] to the nanotube hybrid system, which may in turn enable the addend to be aligned or oriented by convenient external stimuli such as electric field and mechanical shearing.[22] Work along this line is now in progress in our laboratories, in collaboration with the colleagues in our Department of Physics and Center for Display Research.

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