

Degradable Conjugated Polymers: Synthesis and Applications in Enrichment of Semiconducting Single-Walled Carbon Nanotubes

Wei Zhi Wang, Wei Feng Li, Xiao Yong Pan, Chang Ming Li, Lain-Jong Li, Yu Guang Mu, John A Rogers, and Mary B. Chan-Park*

Polymers which enrich semiconducting single-walled carbon nanotubes (SWNTs) and are also removable after enrichment are highly desirable for achieving high-performance field-effect transistors (FETs). We have designed and synthesized a new class of alternating copolymers containing mainchain fluorene and hydrofluoric acid (HF) degradable disilane for sorting and preferentially suspending semiconducting nanotube species. The results of optical absorbance, photoluminescence emission, and resonant Raman scattering show that poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-1,1,2,2-tetramethyldisilane] preferentially suspends semiconducting nanotubes with larger chiral angle (25°-28°) and larger diameter (1.03 nm-1.17 nm) (specifically (8,7), (9,7) and (9,8) species) present in HiPCO nanotube samples. Computer simulation shows that P1 preferentially interacts with (8,7) (semiconducting) over (7,7) (metallic) species, confirming that P1 selects larger diameter, larger chiral angle semiconducting tubes. P1 wrapped on the surface of SWNTs is easily washed off through degradation of the disilane bond of the alternating polymer main chain in HF, yielding "clean" purified SWNTs. We have applied the semiconducting species enriched SWNTs to prepare solution-processed FET devices with random nanotube network active channels. The devices exhibit stable p-type semiconductor behavior in air with very promising characteristics. The on/off current ratio reaches up to 15 000, with on-current level of around 10 μ A and estimated hole mobility of 5.2 cm² V⁻¹ s⁻¹.

Dr. W. Z. Wang, X. Y. Pan, Prof. C. M. Li, Prof. M. B. Chan-Park School of Chemical & Biomedical Engineering Nanyang Technological University 62 Nanyang Drive, Singapore 637459, Singapore E-mail: mbechan@ntu.edu.sg W. F. Li, Prof. Y. G. Mu School of Biological Sciences Nanyang Technological University 60 Nanyang Drive, Singapore 637551, Singapore Prof. L. J. Li Research Center for Applied Science Academia Sinica, Taipei 11529, Taiwan Prof. J. A. Rogers Electrical and Computer Engineering Mechanical and Industrial Engineering Beckman Institute and Frederick Seitz Materials Research Laboratory University of Illinois at Urbana-Champaign Urbana, IL 61801, USA

DOI: 10.1002/adfm.201002278

1. Introduction

Single-walled carbon nanotubes (SWNTs) have attracted a great deal of interest because of their potential applications in electronic devices such as highperformance field-effect transistors, sensors, logic circuits, and electrodes.^[1-5] However, the co-existence of metallic and semiconducting tubes in as-synthesized SWNT samples has been a bottleneck for fundamental research and fabrication of electronic and optoelectronic devices.^[6] It is desirable to develop effective purification methods by which SWNT samples enriched in semiconducting species may be prepared. Various methods to sort semiconducting from metallic nanotubes based on selective chemistry,^[7-15] densitygradient ultracentrifugation,^[16] agarose gel^[17] etc. have been reported.^[18-31]

Methods based on macromolecules such as DNA and aromatic polymers have been demonstrated to be highly effective in selecting a narrow range of species or even single species based on diameter and helicity.^[7–12] Fluorene-based aromatic polymers such as poly(9,9-dioctylfluorenyl-2,

7-diyl) (usually referred to as PFO) have been demonstrated to be diameter- and chirality-selective.^[11] These aromatic polymers have been shown to encase the nanotubes so that the aromatic structures of the nanotube and polymer are aligned and interactions between the π orbitals of SWNT sidewall and polymer are maximized. The nanotube species selection has been found to be highly sensitive to small changes in polymer chemical structure and solvent used.^[12] The versatility of polymer chemistry seems to hold promise for the selection of different specific nanotube species but more understanding is needed.

Significant progress in the selection of specific nanotube species by polymers, as opposed to good dispersion of all species, has only been made in recent years.^[10,11] However, these reports of polymer-based sorting of nanotubes according to chirality or metallicity are mostly based on optical spectroscopy data.^[7–12] There are few reports on the demonstration of reasonably good field-effect transistors (FETs) from these chemically sorted SWNTs. Izard et al.^[32] reported relatively good transistor

FUNCTIONAL www.afm-journal.de $\begin{array}{c} & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & &$

Figure 1. ¹H-NMR spectroscopy of polymer P1, P2, and P3 in CD₃Cl

ppm

4

2

6

8

performance behavior using ultrahigh speed centrifugation of PFO-sorted nanotubes. But highspeed centrifugation (at 150 000g) is necessary and the yield can be expected to be low. It can be reasoned that residual polymer wrapped on the surface of SWNTs, even after extensive washing, results in high inter-tube Schottky barrier and resistance so that connectivity in the SWNTs network is poor. For good transistor performance, there is urgent need for new selective polymers that can be removed easily after the species selection to recover the pristine nanotubes, permitting the creation of SWNT networks with low tube-tube and tube-electrode resistances. Thus far, no such easily removable selective polymers have been reported.

In the research reported in this paper, we designed and synthesized a series of novel easily degradable alternating copolymers of fluorene and disilane, specifically poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-disilane] (Figure 1). The disilane bond is degradable by hydrofluoric acid (HF) washing. The Wurtz-type reductive coupling of dihalodiorganosilanes by sonochemical synthesis has been previously reported for the synthesis of polysilanes with well-controlled molecular weights and low polydispersities.^[33] This method is applied here to synthesize novel copolymers of disilane and fluorene. Specifically, three polymers, PFO-alt-co-(1,1,2,2-tetramethyldisilane), PFO-alt-co-(1,2-dimethyl-1,2-diphenyl-disilane) and PFO-alt-co-(1,1,2,2-tetraphenyldisilane), hereafter denoted P1, P2, and P3, (Figure 1) were synthesized and tested. The synthesized polymers were characterized by ¹H NMR, ¹³C NMR and gel permeation chromatography (GPC). The three polymers (P1, P2, P3) were used to disperse HiPCO SWNTs in toluene. Using photoluminescence (PL) spectroscopy, resonant Raman scattering (RRS) and UV-visible Near Infrared (UV-vis-NIR) spectroscopy, we found that only P1 selects nanotubes with a narrow range of properties (specifically, larger chiral angles, larger diameters and semiconducting). P1 was then washed from the SWNTs after species-sorting by degradation of the disilane bond with HF solution, resulting in "clean" sorted SWNTs. The semiconducting-enriched sample was redispersed in sodium dodecyl

sulfate (SDS) aqueous solution and used to fabricate field-effect transistor (FET) devices. The devices exhibit stable p-type semiconductor behavior in air with very promising characteristics: the on/off current ratio reaches up to 1.5×10^4 , with corresponding on-current level of around 10 µA and estimated hole mobility of 5.2 cm² V⁻¹ s⁻¹. Computer simulations were performed to provide atomic model of P1-SWNT recognition and binding energy analysis confirms the selectivity of P1 for specific semiconducting species.

www.MaterialsViews.com

2. Results and Discussion

2.1. Synthesized Polymers

The P1-P3 chemical structures were confirmed with ¹H-NMR spectroscopy as shown in Figure 1 (see also Supporting Information). All three polymers contain the octylfluorene group, which appears in the spectra as peaks in the ranges 7.7–7.2 ppm (fluorene) and 2.0-0.5 (octyl). Differences among the spectra are due to the different substitution by methyl (-CH₃) or phenyl (Ph) group at Si. In P1, the peak at ~0.35 ppm (peak 'd' in Figure 1) is due to the $-Si(CH_3)$ group present. The spectrum of P3 exhibits no 0.35 ppm peak but has new peaks in the range of 7.2–6.9 ppm (peaks 'e, f, g' in Figure 1) due to the Ph group. The ~7.0 ppm and ~0.35 ppm peaks in P2 are due to the -Si(CH₃)(Ph) group. The GPC profiles of P1, P2, and P3 (Supporting Information) confirm that the dihalodiorganosilane has been successfully incorporated into the polymer structures. The number average molecular weights (M_n) and polydispersity indices of P1, P2, and P3, estimated by GPC against polystyrene standards with THF as an eluent, were about 5600, 4400, and 5200 Daltons and 1.40, 1.37, and 1.47 respectively.

2.2. Optical Spectroscopy

Figure 2 shows the Photoluminescence Excitation (PLE) maps for HiPCO SWNTs dispersed in SDS/D2O and in P1-P3/ toluene. The chiral indices (n,m) for the identified tubes are labeled in the images; the assignments are based on fitting the energy band gaps from the first (E_{11}^{S}) and second (E_{22}^{S}) van Hove transitions to the emission and excitation energies respectively using formulae derived from four-parameter tight binding models.^[34,35] Comparing the PLE peak positions with positions for the corresponding (n,m) species reported in Weisman et al.,^[36] there is a red shift of approximately 1–2% for all four samples. This is due to the effect of the surrounding polymer or SDS on the local dielectric environment. The quantum PL efficiency for each chirality of tube has been reported to be different^[37,38] so that we obtained the individual species abundance from dividing the peak height above the baseline by the species theoretical intensity factor.^[39] The species suspension preferences of the three polymers are summarized in the graphene sheet map of Figure 2e and Table 1.

Figure 2a indicates that HiPCO SWNTs suspended using SDS contain twelve major semiconducting species: (7,5), (7,6), (8,4), (8,6), (8,7), (9,4), (9,5), (9,7), (10,2), (10,3), (10,5), and

JAL

www.afm-journal.de



www.MaterialsViews.com



Figure 2. a-d) PLE maps of SWNTs suspended with polymer dispersants and with SDS in D₂O. e) Graphene sheet map showing dispersant selectivity and efficacy by species. The saturation of the colored circles is proportional to the degree of abundance enhancement inferred from the PLE maps. (The (8,5) cell appears highlighted because all six surrounding cells are highlighted; it is a metallic species and so is not detectable with PLE.)

(12,1). These species range in chiral angle from 3.96° for (12,1) to 28.05° for (9,8) and in diameter from 0.8 nm to 1.2 nm. The corresponding cells in the Figure 2e map are highlighted with orange cell boundaries. It is clear that the SDS/D₂O (deuterium

oxide) shows no apparent chirality preference,^[12] but manifestly solubilizes a wide range of SWNT species. PLE maps of SWNTs suspended with polymers P1–P3 (Figure 2b–d) are dramatically different from the SDS-suspended map. The nanotube species

Table 1. Tabulated values of the relative photoluminescence intensities and relative content for identified species in HiPCO SWNTs dispersed in SDS/ D_2O and P_1 , P_2 , P_3 /toluene solutions.

(n, m)	Diameter [nm]	Chiral angle [deg]	Calculated intensity ^{a)}	PL peak intensity				Calibrated content ^{b)} [%]			
				SDS	P1	P2	P3	SDS	P1	P2	P3
(7,5)	0.829	24.50	0.71	314	239	165	182	2.6	3.1	1.9	1.3
(7,6)	0.895	27.46	0.47	893	271	219	458	11.3	5.4	3.9	5.1
(8,4)	0.840	19.11	0.46	596				7.7			
(8,6)	0.966	25.28	0.49	993	581	413	657	12.1	11.1	7.0	7.0
(8,7)	1.032	27.80	0.30	618	1190	872	892	12.3	36.9	24.0	15.5
(9,4)	0.916	17.48	0.70	1037				8.8			
(9,5)	0.976	20.63	0.28	818			400	17.4			7.5
(9,7)	1.103	25.87	0.27	154	749	556	498	3.4	25.8	17.0	9.6
(9,8)	1.170	28.05	0.19		361	610	641		17.7	26.5	17.6
(10,2)	0.884	8.95	2.38	494				1.2			
(10,3)	0.936	12.73	0.28	695		337	426	14.8		10.0	7.9
(10,5)	1.050	19.11	0.47	409				5.2			
(10,6)	1.111	21.79	0.21			248	269			9.7	6.8
(11,1)	0.916	4.31	0.26				424				8.5
(11,4)	1.068	14.92	0.20				253				6.6
(12,1)	0.995	3.96	0.87	456				3.2			
(12,2)	1.041	7.59	0.2				249				6.6

FULL PAPER

^{a)}Calculated intensity: calculated PL intensity from Oyama et al.^[39]; ^{b)}Calibrated content: PL peak intensity/Calculated intensity

selected by P1-P3 are marked by blue, orange, and green dots respectively in Figure 2e and the color intensity qualitatively correlates to species abundance. Figure 2b shows that P1 preferentially suspends six species: (7,5), (7,6), (8,6), (8,7), (9,7) and (9,8). P1 only suspends SWNT chiral species at the high chiral angle edge of the (n, m) distribution (m = n - 1 or n - 2); these species have large chiral angles (24.5° to 28.1°, blue dots in Figure 2e). P2 suspends eight species, the six suspended by P1 as well as (10,3) and (10,6). The chiral angle of these species ranges from 12.7° for (10,3) to 28.1° for (9,8) (orange dots, Figure 2e). P3 suspends twelve species, i.e., (9,5), (11,1), (11,4), (12,2) and the eight species suspended by P2 (4.3° to 28.1°, green dots in Figure 2e). From the relative abundance of the calculated species (Table 1), it appears that all three polymers strongly select for (8,7), (9,7) and (9,8). These three species account for 80%, 68%, and 43% of the species abundance for P1, P2, and P3, respectively.

PLE is a sensitive method for characterization of the relative abundances of semiconducting SWNTs, but provides no information on the metallic SWNTs content. UV–vis–NIR spectroscopy is sensitive to the presence of metallic species, though it is more difficult to extract precise abundance information from the one-dimensional absorption spectra. As illustrated in **Figure 3**, the pristine (before polymer separation) HiPCO SWNT spectrum shows well-defined peaks corresponding to the (*n*,*m*)-dependent first and second semiconducting [E_{11}^{S} (870–1600 nm) and E_{22}^{S} (550–870 nm)], and first metallic [E_{11}^{M} (440–670 nm)] optical transitions, typical of individually suspended or small bundle nanotubes. Metallic species such as (7,7), (8,5), (9,9), (10,7), (11,5) and (13,4), which have been shown to be present in HiPCO^[40] are detected. After polymer separation, the ratio of peaks in E_{11}^{M} region to E_{22}^{S} obviously decreased, indicative of the decreasing content of metallic nanotube species. Also, after polymer separation, the ratio of semiconducting (8,7) species increases and that of (7,6) decreases, which corroborate the PLE results (Figure 2e).

To investigate the species selectivity by P1 polymer, RRS spectroscopy using three different excitation lasers (785 nm, 633 nm and 514 nm) was employed. Different laser wavelengths bring different tube species into resonant scattering since the energy of the species interband electronic transition depends on its



Figure 3. Absorbance spectra of SWNTs dispersed in SDS/D_2O (2 wt%). a) Before and b) after polymer (P1) separation.



www.MaterialsViews.com



Figure 4. Raman spectra of P1-enriched SWNTs under a–b) 785 nm, c–d) 633 nm, and e–f) 514 nm excitation.

diameter and metallicity. The spectra of P1-suspended SWNTs are shown in **Figure 4**. The chirality of nanotubes in the radial breathing mode (RBM) in Figure 4 has been assigned according to experimental Kataura plot.^[41,42] (It should also be noted that shift curves due to discrete Raman excitation wavelengths cannot show all the metallic or semiconducting species.)

Using the 785 nm excitation laser, the RMB peaks of pristine and P1-separated samples are different (Figure 4a). Before separation by P1, the pristine SWNTs contain relatively large amounts of (7,5) and (7,6) compared to the larger diameter (8,6) and (8,7) species. However, after separation with P1, the ratio is reversed: (8,6) and (8,7) becomes relatively more abundant than (7,5) and (7,6). These results are also corroborated by the PLE spectra (Figure 2e, P1). In the 633 nm excitation spectrum (Figure 4c), the RBM of pristine SWNTs above 240 cm⁻¹ arises from semiconducting tubes which include (7,5), (7,6), and (8,6) species (which are also detected by PLE (Figure 2e, P1). RBM features below 240 cm⁻¹ are due to metallic nanotubes, mainly the (13,4) and (11,5) species. After P1 separation, the metallic (13, 4) peak disappears and (11,5) significantly decreases in intensity. The Raman results for the identified species are corroborated by the UV-vis-NIR results. Figure 4e shows the Raman RBM spectra with 514 nm excitation. The two spectra (pristine and P1-separated) are normalized at the G^+ peak (at around 1580 cm⁻¹, Figure 4f). The peaks from 220 to 270 cm^{-1} can be assigned to the metallic (7,7), (8,5) and (9,3) species and these peaks decrease in intensity after P1 separation, indicating reduced abundance of these species. These 514 nm Raman results are corroborated by the corresponding reduced E_{11}^{M} peak in the UV-vis–NIR spectrum (Figure 3). The reduction in metallic species abundance after P1 selection is also corroborated by the slightly reduced intensities of the G⁻ bands (at around 1550 cm⁻¹) for the three

FUNCTIONAL MATERIALS www.afm-journal.de FUNCTIONAL MATERIALS ______ www.afm-journal.de



Figure 5. Structure topology of $P1_{(15)}$ with a) SWNT (8,7) and b) SWNT (7, 7).

excitation wavelengths compared to those of pristine nanotubes (Figures 4b, d and f). The G⁻ band due to metallic tubes has a Breit–Wigner–Fano line shape, and is broader and downshifted in frequency from semiconducting tubes of similar diameter.

2.3. Computer Simulation of P1 Wrapping and Selectivity

The PL spectroscopy tests show that P1 enriches a specific range of larger chiral angle (25.8°–28.1°) and larger diameter (1.0 nm–1.2 nm) semiconducting nanotubes. The 514 nm Raman results (Figure 4e, f) show that the (7,7) metallic arm-chair species is not preferred by P1 so that P1 selects the larger chiral angle but not armchair (30°) nanotubes. Taken together, P1 seems to enrich larger diameter and larger chiral angle semiconducting nanotubes.

All-atomic molecular dynamics simulations were employed to study the interaction pattern between P1 polymer molecule and representative metallic and semiconducting species: (7,7) and (8,7) species respectively. Simulations began with a small fragment of P1 which contains 3 repeating units of P1 molecule, named P1(3) hereafter. Initially, the P1(3) molecule was placed about 1.5 nm from the SWNT. 30 ns simulations were performed for P1(3) in interaction with a segment of (7,7) and (8,7) SWNT separately. Based on the binding pattern of $P1_{(3)}$ on (8,7) species, the P1(3) molecule was extended by four additional copies around the SWNT, forming a SWNT(8,7) helicallywrapped with P1(15). This model was equilibrated in explicit toluene solvent for 40 ns and the final simulated structure is shown in Figure 5. From the side-view (Figure 5a), each unit in P1(15) wraps around (8,7) species adopting an nearly identical helical angle relative to (8, 7) SWNT. A simulation study of P1(15) on (7,7) SWNT was also performed. An equilibrated structure of P1(15) wrapped around (7,7) SWNT shown in Figure 5b demonstrates also a helical pattern. To predict the binding strength of P1(15) molecule with the two types of SWNTs, the binding energy of SWNT-P1(15) complex is calculated as:

$$E_B = E_{complex}^{GB} - E_{CNT}^{GB} - < E_{P1(15)}^{GB} >$$
(1)

where $E_{complex}^{GB}$, E_{CNT}^{GB} and $< E_{P1(15)}^{GB} >$ are the energies of SWNT-P1₍₁₅₎ complex and SWNT respectively and average



energy of a helically-patterned P1₍₁₅₎, based on the implicit generalized Born (GB) model. At the end of 40 ns simulations, the binding energy of P1₍₁₅₎ with (8,7) SWNT is about 33.8 kcal mol⁻¹ lower than that with a (7,7) SWNT (see Supporting Information, Figure S4). The binding energies calculated indicate that P1₍₁₅₎ favors (8,7) SWNT over (7,7) SWNT, so that P1 preferentially selects semiconducting (8,7) over (7,7).

2.4. SWNT-Based FETs

The strongest proof of semiconducting nanotube enrichment by P1 is in the application of the enriched SWNTs as the active material in thin film FETs. Network FETs were made by drop-casting nanotube solution in the FET channel. The geometry of our fabricated bottom-gated FETs is shown in the Supplementary Information. After the enrichment process by P1, the P1-suspended nanotubes were filtered and then HF was used to degrade the residual P1 polymer on the tubes before applying them to make FETs. FTIR characterization of the P1-selected HF-cleaned SWNTs confirms the removal of P1 (Supporting Information). Pristine HiPCO SWNTs were also applied to make FETs for comparison. SWNT solution droplets were added onto the channel area until the resistance of the device was less than $\sim 1 \text{ M}\Omega$. The SWNT network in the channel was characterized with atomic force microscopy (AFM). Figure 6a shows a 4 μ m × 4 μ m scan of the SWNT network in the device channel. The measured areal density of nanotubes in the channel area is about 10–20 tubes μ m⁻². Figure 6b shows the typical transfer characteristics with forward sweep of drain current (I_d) versus gate voltage (V_g) for a bottom-gated FET made with HF-cleaned SWNTs enriched using P1; the device exhibits a typical p-type behavior and has an effective carrier mobility of 5.2 cm² V⁻¹ s⁻¹ and on/off ratio of 1.5×10^4 .

Figure 6c is a histogram of the on/off ratios for devices constructed with pristine HiPCO (using SDS suspended in H₂O) and P1-selected HF-cleaned SWNT solutions. All devices made from the P1-selected HF-cleaned SWNT solution exhibit on/off ratios ranging from 1 000 to 100 000 and effective mobilities in the range 3 to 5 cm² V⁻¹ s⁻¹. Devices made with pristine SWNTs had very low on/off ratios in the range of 1 to 10.

Figure 6d shows the dependence of on/off ratio and on-state current on the SWNT areal density in the active channel. The nanotube densities were measured with AFM. Very sparse films (1 to 4 SWNT μ m⁻²) do not form sufficient conduction paths to yield measurable on-state current. Owing to efficient removal of most of the metallic SWNTs with P1, it is possible to increase the density (thickness) of the networks without building up excessive metallic SWNT conduction paths. The on current increases linearly from 4 µA to 13 µA as the SWNT density varies from 7 to 60 μ m⁻². The on/off ratio decreases exponentially with increasing SWNT density. The decline in on/off ratio implies the presence of some metallic SWNTs though the metallic SWNT content in our sample is quite low (around 9% after P1 enrichment). Also, these results demonstrate that it is possible to tune the mobility of solution-processed SWNT transistors by controlling the density of the SWNT films.

To demonstrate the importance of the degradability of the polymer on device performance, devices were made with



Figure 6. a) AFM images of SWNT network in the channel. b) Typical FET transfer characteristic. c) Histogram of FET on/off ratios. d) FET on/off ratio and on-state current versus SWNT density in the active channel.

SWNTs that had been P1-selected but not cleaned with HF solution. These devices had low on currents (usually around 10^{-8} A), although the metallic species were significantly depleted as evidenced by the spectroscopy data. We interpret this to be evidence that the SWNTs were still wrapped with polymer chains, which increased the Schottky barrier and reduced the on current and the on/off ratio. Comparison of the on/off ratios of FETs made with P1-selected SWNTs with and without HF-cleaning suggests that the removal of impurities (ash and catalyst) may not be the most important factor to achieve high-performance devices. Removal of the organic dispersion/selection agent from the semiconducting SWNTs enriched sample prior to device fabrication is crucial to obtain good on/off ratio and mobility characteristics.

Some experimental details employed in the FET fabrication to improve device performance and repeatability are worthy of mention. Firstly, the wafer surface was treated with oxygen (O_2) plasma. This is expected to improve contacts between SWNTs and the electrodes. It may also promote adhesion of SWNTs to the wafer surface. O_2 plasma treatment renders the substrate and electrode surfaces hydrophilic. Secondly, during the droplet evaporation, fluid flow in the droplet tends to cause the SWNTs to migrate to the edges of the droplet – the coffee-ring effect. This reduces the density of nanotubes in the channel region. This effect may be counteracted by positioning a permanent magnet beneath the substrate during droplet evaporation. Thirdly, we improved the alignment, and thus the network connectivity, of the SWNTs along the channel direction by depositing the solution on one side of the device and blowing the solution droplet across the device. This set up a circulation in the droplet that tended to align the SWNTs in the desired direction. A significant degree of alignment was obtained by this means (see Supporting Information). We found this method to improve the on current by about 25%.

The strong binding of the flexible P1 main chain wrapped helically on semiconducting and large chiral angle, large diameter nanotube species (specifically (8,7), (9,7), (9,8)) enables the polymer to provide buoyant force even under centrifugation to stabilize the selected species. The helical P1 would have a preferred core diameter corresponding to minimum energy so that specific diameter SWNTs (1.0 nm–1.2 nm) are encased and chosen. Specific chiral angle (25° to 28°) nanotubes optimize the alignment of aromatic structures of the nanotubes and P1 polymer. The specific chiral angle and diameter of nanotubes



selected by P1 dictate the enrichment of semiconducting species. The UV-vis–NIR and Raman spectroscopy results, improved FET performance, and computer simulation show that the P1 enriches semiconducting large chiral angle, large diameter nanotubes. The degradation of our polymer enables the nanotubes to be fairly "clean" resulting in low intertube resistance and high performance devices.

Being stiffer, P3 poorly wraps or stacks on the surface of SWNTs, unlike the wrapping interaction of P1. Since P3 is less able to conform to the SWNT surface, it is expected to be less discriminating among different tube species. A stable model of P3/SWNT in solution would be several chains surrounding but not conforming to the nanotube. The behavior of P2 may be intermediate between those of P1 and P3.

3. Conclusion

We have designed and synthesized a new class of alternating copolymers, P1, P2, and P3, which contain fluorene and HF-degradable disilane in the main chain, for use as agents for the dispersion and enrichment of SWNTs. Optical absorbance, photoluminescence, and Raman scattering spectroscopy show that only P1 is effective in selecting specific nanotube species. P1 is highly selective for higher chiral angle (25° to 28°) and larger diameter (1.0 nm – 1.2 nm) semiconducting tubes, specifically (8,7), (9,7), and (9,8) SWNTs (which constitute above 80% of all semiconducting tubes). Computer simulation shows that the P1 molecule can wrap around SWNT in a helical pattern and binding energy analysis confirms the preferable binding of P1 onto semiconducting (8,7) species over metallic (7,7) species.

P1 wrapped on the SWNT surfaces can be easily removed by degradation of the polymer chain in HF solution to yield "clean" SWNTs. We applied the semiconducting-enriched SWNTs to fabricate field-effect transistor (FET) devices based on random nanotube networks. The devices exhibit stable p-type semiconductor behavior in air with very promising characteristics. The on/off current ratio reaches up to 15 000 with corresponding on-current level of around 10 μ A, and estimated hole mobility of 5.2 cm² V⁻¹ s⁻¹.

4. Experimental Section

Materials: Chemicals and reagents were purchased from Aldrich and Acros Chemical Co., unless otherwise stated, and used without further purification. When necessary, the solvents were purified according to conventional methods. SWNTs synthesized by the "HiPCO" growth process^[43] and with quoted purities of >85% were purchased from Carbon Nanotech. Inc (Batch No. SP0333). The nanotubes were used as purchased.

Synthesis of 2,7-bis(chlorosilyl)-9,9-dioctylfluorene: Into a solution of 2,7-dibromo-9,9-dioctylfluorene (6.52 g, 14.0 mmol) in anhydrous THF (100 mL) was added n-BuLi (2.5 M in hexane, 11.2 mL, 28.0 mmol) at -78 °C in 30 min. The reaction mixture was stirred for 1 h before adding one of the three listed chemicals (dichlorodimethylsilane (Me₂SiCl₂), dichloromethylphenyl-silane (MePhSiCl₂) or dichlorodiphenylsilane (Ph₂SiCl₂)) (15.0 mmol) for P1, P2 or P3, respectively. The mixture was warmed to room temperature and then stirred for 30 min. Upon evaporation of the solvent, the residue was a colorless liquid.

Ultrasound Synthesis of Polymer: A 50-mL, three-necked, round-bottom flask was fitted with a reflux condenser and a pressure-equalizing addition

funnel. All systems were thoroughly flame-dried under nitrogen. Known amounts of sodium (0.3 g) were added to the flask, which was filled with 30 mL of toluene and purged with dry nitrogen. Sodium particles were irradiated with ultrasound until a stable dispersion of sodium was formed. After irradiation for approximately 1 h at 60 °C, a mixture of dichlorosilanes in toluene (8 mL) was added dropwise to the reaction flask in a controlled manner (3 drops min⁻¹) under argon. The above prepared 2,7-bis (chlorosilyl)-9,9-dioctylfluorene was added to the flask within 15 min, and the reaction mixture turned from grey to dark purple after 2 min. The organic phase was later added to a large excess (250 mL) of isopropyl alcohol, leading to the precipitation of the polymer. The white precipitate was collected by centrifugation and dried overnight at 60 °C in vacuum.

Measurements and Characterization: ¹H NMR and ¹³C NMR spectra were recorded with a Bruker DMX-3000 spectrometer, and chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. UV-vis-NIR absorption spectra were measured on a Varian Cary 5000 UV-vis-NIR spectrophotometer. GPC was performed with an Agilent 1100 Series equipped with GPC-SEC (size exclusion chromatography) data analysis software. PLE spectroscopy measurements were conducted with a Jobin-Yvon Nanolog-3 spectrofluorometer. Correction for variations in the lamp spectral response was made using a silicon photodiode. Raman spectra were collected with a Renishaw Raman scope in backscattering configuration using 785 nm, 633 nm, and 514 nm laser wavelengths over five random spots on SWNT solid samples. Laser power of 2.5-5.0 mW was used to prevent destruction of the SWNT samples during measurement. AFM was conducted using a MFP 3D microscope (Asylum Research, Santa Barbara, CA) with a cantilever (Arrow NC, Nanoworld) in ac mode. The scan rate was set to 1 Hz at various scan sizes.

Purification of SWNTs with Degradable Polymers: The preparation of the polymer-SWNT dispersion in toluene has been reported elsewhere.^[10,12,44] In brief, crude SWNT powders were dispersed in polymer/toluene solutions in the ratio SWNT (5 mg): polymer (5–20 mg): toluene (50 mL). The solutions were then homogenized in a sonic bath for 30 min followed by probe sonication (Sonics & Materials Inc., model VCX 130, 80 Watts) for 30 min, and then promptly followed by centrifugation at 20 000 g for 5 min. The supernatant was filtered with Teflon filters (200 nm pore size). The recovered solids were dispersed in a HDPE bottle with DMF (15 mL) and HF (1 mL) solution (40 wt%, 22.77 mol) mixture for 10 hours to degrade the polymer. The solution was then diluted with water and filtered with Teflon filters (200 nm pore size). The resulting "clean" SWNTs were thoroughly washed with THF until the signal of fluorene completely disappeared in thin layer chromatography.

FET Fabrication and Characterization: SWNT thin film FETs were fabricated by the drop-casting method. Semiconducting-enriched "clean" SWNTs were dispersed in 1 wt% SDS water solution and the concentration was adjusted by adding SDS surfactant solution until the resultant solution UV-vis-NIR absorbance at 950 nm was 0.02.^[45] The resulting SWNT dispersions were dropped on electrode-patterned substrates to form bottom-contact FET devices (see Supporting Information). Au electrodes (40 nm thick) were pre-patterned on SiO₂/ Si substrates, with Ti as adhesion layer, using standard lithography techniques. The SiO₂ gate dielectric was 300 nm thick. The FET device channel was 20 μm long and 60 μm wide. The SWNT network active channel of each device was formed by drop-casting 10 µL of SWNT suspension, followed by drying and rinsing with deionized water. To improve the SWNT film uniformity, the channel area was treated with O_2 plasma (100 W) for 3 min before application of the SWNT dispersion. The treatment of device surfaces with O2 plasma helps to limit the "coffeering" effect.^[46] All electrical measurements were carried out in ambient environment using a Keithley semiconductor parameter analyzer model 4200-SCS. The effective field-effect mobility (μ) was estimated by:

$$\mu = 10^4 \times \frac{I_d}{V_{gs}} \times \frac{L}{W} \times \frac{1}{C_{ox}V_{ds}}$$
(2)

where C_{ox} is determined by $\varepsilon_0 \varepsilon_r A/d$, where ε_0 is permittivity of free space (8.85 × 10⁻¹²), ε_r is relative permittivity of SiO₂ (3.9), A is unit area and





www.MaterialsViews.com

d is the thickness (3 × 10⁻⁷) of the gate silicon oxide. *L* and *W* represent the channel length and width, respectively. *I*_d, *V*_{ds} and *V*_{gs} are the drain current, drain voltage and gate voltage respectively.

Theoretical Calculations: To explore the atomic interaction mechanism between specific SWNT species and P1 polymer in toluene, all-atomic molecular dynamics simulations were performed. Generalized Amber force fields were used. All the simulations were done with GROMACS package with the help of Amb2gmx utility tool. The atomic charges of toluene and P1 were generated from quantum calculations with Gaussian03 with B3LYP/6–31G basis. Two SWNT chiralities, (7, 7) and (8, 7), were studied.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The work was supported by a Competitive Research Program grant from the Singapore National Research Foundation (NRF-CRP2-2007-02).

Received: October 28, 2010

Revised: January 6, 2011

Published online: March 22, 2011

- J. Kong, N. R. Franklin, C. W. Zhou, M. G. Chapline, S. Peng, K. J. Cho, H. J. Dai. *Science* **2000**, *287*, 622.
- [2] A. Bachtold, P. Hadley, T. Nakanishi, C. Dekker. Science 2001, 294, 1317.
- [3] M. Shim, M. Cao. Adv. Mater. 2006, 18, 304.
- [4] Z. H. Chen, J. Appenzeller, Y. M. Lin, J. S. Oakley, A. G. Rinzler, J. Y. Tang, S. J. Wind, P. M. Solomon, P. Avouris. *Science* **2006**, *311*, 1735.
- [5] H. E. Unalan, G. G. Fanchini, A. A. Kanwal, A. A. Du Pasquier, M. M. Chhowalla. Nano Lett. 2006, 6, 677.
- [6] M. A. Topinka, M. W. Rowell, D. G. Gorden, M. D. McGehee, D. S. Hecht, G. Gruner. Nano Lett. 2009, 9, 1866.
- [7] X. M. Tu, S. Manohar, A. Jagota, M. Zheng. Nature 2009, 460, 250.
- [8] M. Zheng, B. A. Dinner. J. Am. Chem. Soc. 2004, 126, 15490.
- [9] M. Zheng, A. Jagota, E. D. Semke, B. A. Dinner, R. A. Lustig, R. E. Richardson, N. G. Tassi. *Nat. Mater.* **2003**, *2*, 338.
- [10] F. Chen, B. Wang, Y. Chen, L. J. Li. Nano Lett. 2007, 7, 3013.
- [11] A. Nish, J. Y. Hwang, J. Doig, R. J. Nicholas. Nat. Nanotechnol. 2007, 2, 640.
- [12] J. Y. Hwang, A. Nish, J. Doig, S. Douven, C. W. Chen, L. C. Chen, R. J. Nicholas. J. Am. Chem. Soc. 2008, 130, 3543.
- [13] R. Marquis, C. Greco, I. Sadokierska, S. Lebedkin, M. M. Kappes, T. Michel, L. Alvarez, J. L. Sauvajol, S. Meunier, C. Mioskowski. *Nano Lett.* 2008, *8*, 1830.
- [14] R. M. Tromp, A. Afzali, M. Freitag, D. B. Mitzi, Z. Chen. Nano Lett. 2008, 8, 2, 469.
- [15] S. Y. Ju, J. Doll, I. Sharma, F. Papadimitrakopoulos. *Nat. Nanotechnol.* 2008, *3*, 356–362.
- [16] M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp, M. C. Hersam. Nat. Nanotechnol. 2006, 1, 60.
- [17] T. Tanaka, H. Jin, Y. Miyata, S. Fujii, H. Suga, Y. Naitoh, T. Minari, T. Miyadera, K. Tsukagoshi, H. Kataura. *Nano. Lett.* **2009**, *9*, 1497.
- [18] K. H. An, J. S. Park, C. M. Yang, S. Y. Jeong, S. C. Lim, C. Kang, J. H. Son, M. S. Jeong, Y. H. Lee. J. Am. Chem. Soc. 2005, 127, 5196.

- [19] Z. Xu, W. Lu, W. Wang, C. Gu, K. Liu, X. Bai, E. Wang, H. Dai. Adv. Mater. 2008, 20, 3615.
- [20] M. S. Strano, C. A. Dyke, M. L. Usrey, P. W. Barone, M. J. Allen, H. Shan, C. Kitrell, R. H. Hauge, J. M. Tour, R. E. Smalley. *Science* 2003, 301, 1519.
- [21] J. Zhao, C. W. Lee, X. Han, F. Chen, Y. Xu, Y. Huang, M. B. Chan-Park, P. Chen, L. J. Li. *Chem. Commun.* **2009**, 7182.
- [22] H. Zhang, Y. Liu, L. Cao, D. Wei, Y. Wang, H. Kajiura, Y. Li, K. Noda, G. Luo, L. Wang, J. Zhou, J. Lu, Z. Gao. *Adv. Mater.* **2009**, *21*, 813.
- [23] Y. Miyata, Y. Maniwa, H. Kataura.J. Phys. Chem. B 2006, 110, 25.
- [24] R. Krupke, F. Hennrich, H. Lohneysen, M. Kappes. Science 2003, 301, 344.
- [25] R. Krupke, S. Linden, M. Rapp, M. Kappes. Adv. Mater. 2006, 18, 1468.
- [26] P. Stokes, S. I. Khondaker. Nanotechnology 2008, 19, 175202.
- [27] H. Li, B. Zhou, L. Gu, W. Wang, K. A. S. Ferando, S. Kumar, L. F. Allard, Y. P. Sun. J. Am. Chem. Soc. 2004, 126, 1014.
- [28] W. Wang, K. A. Fernando, Y. Lin, M. J. Meziani, L. M. Veca, L. Cao, P. Zhang, M. M. Kimani, Y. P. Sun, J. Am. Chem. Soc. 2008, 130, 1415.
- [29] L. Wei, B. Wang, T. H. Goh, L. J. Li, Y. Yang, C. P. Chan, Y. Chen, J. Phys. Chem. B 2008, 112, 2771.
- [30] Y. Maeda, S. I. Kimura, M. Kanda, Y. Hirashima, T. Hasegawa, T. Wakahara, Y. Lian, T. Nakahodo, T. Tsuchiya, T. Akasaka, J. Lu, X. Zang, H. Tokumoto, R. Saito, J. Am. Chem. Soc. 2005, 127, 10287.
- [31] Z. Chen, X. Du, M. Du, C. Rancken, H. Cheng, A. Rinzler, Nano Lett. 2003, 3, 1245.
- [32] N. Izard, S. Kazaoui, K. Hata, T. Okazaki, T. Saito, S. Iijima, N. Minami, Appl. Phys. Lett. 2008, 92, 243112.
- [33] W. Z. Wang, Q. L. Fan, F. Cheng, P. Zhao, W. Huang, J. Polym. Sci., Polym. Chem. Ed 2006, 44, 3513.
- [34] M. S. Strano, S. K. Doorn, E. H. Haroz, C. Kittrell, R. H. Hauge, R. E. Smalley, *Nano Lett.* 2003, *3*, 1091.
- [35] L. J. Li, T. W. Lin, J. Doig, I. B. Mortimer, J. G. Wiltshire, R. A. Taylor, J. Sloan, M. L. H. Green, R. J. Nicholas, *Phys. Rev. B* 2006, 74, 245418.
- [36] S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley, R. B. Weisman, *Science* **2002**, *298*, 2361.
- [37] S. Reich, C. Thomsen, J. Robertson, Phys. Rev. Lett. 2005, 95, 077402.
- [38] Z. Luo, L. D. Pfefferle, G. L. Haller, F. Papadimitrakopoulos, J. Am. Chem. Soc. 2006, 128, 15511.
- [39] Y. Oyama, R. Saito, K. Sato, J. Jiang, G. G. Samsonidze, A. Gruneis, Y. Miyauchi, S. Maruyama, A. Jorio, G. Dresselhaus, M. S.*Carbon* 2006, 44, 873.
- [40] E. H. Hároz, W. D. Rice, B. Y. Lu, S. Ghosh, R. H. Hauge, R. B. Weisman, S. K. Doorn, J. Kono, ACS Nano 2010, 4, 1955.
- [41] C. Fantini, A. Jorio, M. Souza, M. S. Strano, M. S. Dresselhaus, M. A. Pimenta, *Phys. Rev. Lett.* **2004**, *93*, 147406.
- [42] J. Maultzsch, H. Telg, S. Reich, C. Thomsen, Phys. Rev. B 2005, 72, 205438.
- [43] P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T. Colbert, K. A. Smith, R. E. Smalley, *Chem. Phys. Lett.* **1999**, *313*, 91.
- [44] W. Yi, A. Malkovskiy, Q. Chu, A. P. Sokolov, M. L. Colon, M. Meador, Y. Pang, J. Phys. Chem. B 2008, 112, 12263.
- [45] L. Wei, C. W. Lee, L. J. Li, H. G. Sudibya, B. Wang, L. Q. Chen, P. Chen, Y. Yang, M. B. Chan-Park, Y. Chen, *Chem. Mater.* **2008**, *20*, 7417.
- [46] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, T. A. Witten. *Nature* **1997**, *389*, 827.