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Toward the Extraction of Single Species of Single-Walled Carbon Nanotubes Using Fluorene-Based Polymers

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ABSTRACT

High purity of (7,5) SWNTs (∼79% of the semisonducting SWNT ensemble) can be obtained by polymer-assisted extraction from the narrow-diameter distributed SWNTs produced by the catalyst Co-MCM-41. The fluorene-based polymers are able to selectively wrap the single-walled carbon nanotubes (SWNTs) with certain chiral angles or diameters depending on their chemical structures. Poly(9,9-dioctyfluoreny1–2, 7-diyl) and poly[(9,9-dihexylfluorenyl-2,7-diyl)-*co*-(9,10-anthracene)] selectively wrap SWNTs with high chiral angles (>24.5°). By contrast, poly[9,9-dioctylfluorenyl-2,7-diyl)-*co*-1,4-benzo-{2,1′-3}-thiadiazole)] preferentially wraps the SWNTs with certain diameter (1.02–1.06 nm).

Much attention has been paid to single-walled carbon nanotubes (SWNTs) due to their high mechanical strength, excellent electrical properties, and unique electronic band structures. SWNTs have a high potential for future applications in the fields of energy, electronics, and sensing applications. However the coexistence of tubes with various chiralities in commercially available SWNTs has been a bottleneck for fundamental research and fabrication toward high-performance devices. It is therefore desirable to develop the selective synthesis and purification methods that allow us to obtain chiral specific SWNT samples.

We have developed the catalyst system of Co-incorporated mobile composition of matter 41 (Co-MCM-41) to grow narrowly diameter distributed SWNTs.[1−3] This method has produced one of the narrowest (*n*,*m*) distributed SWNTs thus far.[4] However, it will be very difficult to get high purity of single-species SWNT samples from any synthesis technique alone. Follow-on separation techniques need to work hand-in-hand with selective synthesis to achieve such a goal. Several methods have been reported to enrich semiconducting or metallic SWNTs such as octadecylamine assisted precipitation,[5] oxidation,[6] and selective chemical functionalization by nitronium ion,[7] bromination,[8] and fluorination.[9] These methods involve chemical attachments onto SWNTs and therefore change the electronic structure of SWNTs. Direct electrical breakdown[10] of metallic tubes on SWNT devices has also been reported to improve the on−off characteristics, where the reproducibility is still a challenge. Dielectrophoresis[11−12] and density gradient assisted separation[13−14] have demonstrated the possibilities toward nondestructive enrichment in metallic, certain diameter or certain length of tubes. We also notice that some specific semiconducting SWNTs ((6,5) and (7,5)) have been significantly enriched by using density gradient assisted separation.[14] Another attractive approach is by deoxyribonucleic acid (DNA) assisted dispersion[15−16] or polymer wrapping,[17] where the selectivity is from the stability of the SWNT−DNA or SWNT−polymer complex in solutions. We were aware that poly(9,9-dioctyfluoreny1-2,7-diyl) (PFO) might have a high preference for wrapping the SWNTs with large chiral angles.[18] We then studied the selective wrapping of SWNTs by using various fluorene-based polymers from narrow diameter distributed SWNT samples. Here we report that high purity of (7,5) SWNTs can be obtained by extraction from SWNTs produced by Co-MCM-41. However, such high selectivity cannot be obtained on wide diameter distributed SWNT samples, although some of the polymers can selectively wrap the SWNTs with certain chiral angles or diameters depending on their chemical structures.

PFO, poly[(9,9-dihexylfluorenyl-2,7-diyl)-*co*-(9,10-anthracene)] (PFH-A), and poly[9,9-dioctylfluorenyl-2,7-diyl)-*co*-1,4-benzo-{2,1′-3}-thiadiazole)] (PFO-BT) were purchased from American Dye Source Inc., and their chemical structures are shown in Figure 1. The narrow diameter distributed SWNTs (labeled as CoMCM SWNTs) were produced by chemical vapor deposition based on CO disproportionation on Co-MCM-41 catalysts.[1−3] For reference

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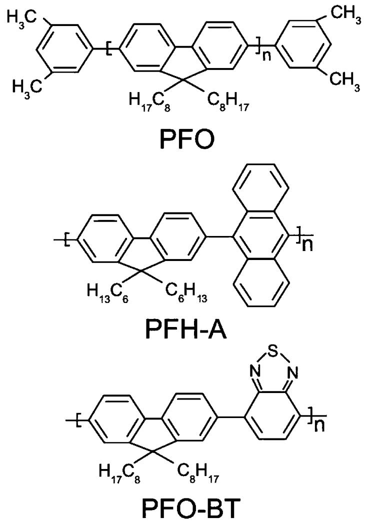

Figure 1. Chemical structures of PFO, poly[(9,9-dihexylfluorenyl-2,7-diyl)-*co*-(9,10-anthracene)] (PFH-A), and poly[9,9-dioctylfluorenyl-2,7-diyl)-*co*-1,4-benzo-{2,1′-3}-thiadiazole)] (PFO−BT).

optical measurements, the obtained SWNTs (before separation) were dispersed in aqueous sodium dodecylbenzene sulfate (SDBS) suspensions with 30 min of probe sonication (Sonics & Materials Inc., model VCX 130), followed by ultracentrifugation at 53 000*g*. Typical procedures for SWNT extraction using polymers were as follows: The nanotube powders were dispersed in polymer/toluene solutions in the ratio 3 mg SWNT:5−25 mg polymer:8 mL solvent. The solutions were then homogenized in a sonic bath for 30 min, followed by probe sonication for 3−15 min. This was then promptly followed by centrifugation at 11 000*g* for 3 min. Absorbance measurements were taken by using a Perkin-Elmer Lambda 900 photospectrometer. Photoluminescence excitation (PLE) mapping was performed by using a Jobin-Yvon Horiba Fluorolog-3 spectrophotometer with fluorEssence software.

Parts a and b of Figure 2 show the PLE mappings for the CoMCM SWNTs dispersed in SDBS/D_2O and in PFO/toluene, respectively. The chiral indices (n,m) for the identified tubes were labeled on the graphs, where the assignment was based on fitting the energy band gaps from the first (E_{11}^{S}) and second (E_{22}^{S}) van Hove transitions for the tubes using the formulas derived from four-parameter tight-binding models.[19−20] Table 1 summarizes the relative content of the identified semiconducting species from PLE for both SDBS and PFO wrapped tubes. The intrinsic PL efficiency for each chirality of tube is different, as reported in the literature,[21−23] therefore we calculate the relative content of each tube based on the calibrated PL intensity (dividing the experimental PL intensity by calculated PL intensity),[22] where the experimental PL intensity is determined from the amplitude of the partial derivative of the PLE map, as suggested by Arnold et al.[14] to minimize the effect of the slowly varying background. It is observed that the CoMCM SWNTs are composed of four major semiconducting species (8,4), (7,5), (7,6), and (6,5) in SDBS suspension, whereas only high chiral angle species (≥24.5°; (7,5) and (7,6)) are selectively wrapped in PFO/toluene suspension. Noted that the PFO is found to preferentially wrap the tubes with high chiral angle tubes and certain diameter (0.76−1.03 nm) (Supporting Information Table S1). The last column "ratio" in Table 1 lists the ratio of the content in PFO/toluene to that in SDBS/D_2O suspension, which gives an idea in the extraction ability of PFO for each species. Figure 2c illustrates the wrapping preference of PFO using chirality map, where the thick and filled hexagons present the species identified in SDBS/D_2O and PFO/toluene suspension, respectively. The filled hexagon with thicker color indicates the tube species with higher preference being wrapped. The dominant species in PFO suspension is (7,5), which contributes to ∼79% of the semiconducting ensemble. The optical absorption spectra for CoMCM SWNTs dispersed in PFO/toluene solutions (Supporting Information Figure S1) also confirm that the number of species is largely reduced after wrapping. We realize that the purity after one extraction of (7,5) using PFO and CoMCM SWNTs is already higher than the 60% from three iterations of density differentiation.[14] It is also noted that, to obtain such a high purity of single species, it is necessary to use narrow diameter distributed SWNTs (e.g., CoMCM SWNTs in this case) as starting materials.

For comparison, we have also studied the fluorene-based polymers wrapping process by using the SWNTs produced by high-pressure CO process (HiPCO) (with more species compared with CoMCM SWNTs). We can only obtain ∼12% of (7,5), and the major species obtained are (8,6) and (8,7) due to the fact that the HiPCO tubes are composed of many other high chiral angle species. Figure 3a shows the PLE mapping for the HiPCO SWNTs dispersed in SDBS/D_2O, where at least 17 semiconducting species are identified. Parts b−d of Figure 3 show the PLE mappings for HiPCO tubes dispersed in toluene by PFO, PFH-A, and PFO-BT, respectively. Similar analysis for the content of each species before and after polymer extraction is listed in Supporting Information Tables S1−S3. Figure 3f illustrates the wrapping preference of PFO, PFH-A, and PFO−BT by using a chirality map, where only major species are plotted for simplicity. We observe that PFO and PFH-A have similar selectivity in wrapping high chiral angle tubes (>21.8°), whereas PFH-A has higher preference in solublizing larger diameter tubes (0.97−1.17 nm) compared with PFO (0.83−1.03 nm), which further provides a possibility to extract various diameter tubes with similar chiral angle. By contrast, PFO-BT demonstrates high wrapping selectivity in tube diameter (1.03−1.07 nm) rather than chirality. It is noted that the relative percentage of (10,5) among all identified semiconducting species is ∼53% (Supporting Information Table S3).

We have repeated the extraction at least 5 times for each polymer. PLE and absorption spectra obtained in all cases are reproducible. One issue of the wrapping process using fluorine-based polymers we have noticed is that the wrapping efficiency is not very high. However, the efficiency can be improved by increasing the polymer concentration in solution. So far the highest wrapping efficiency we have obtained for the case of HiPCO tubes in PFO/toluene system is around

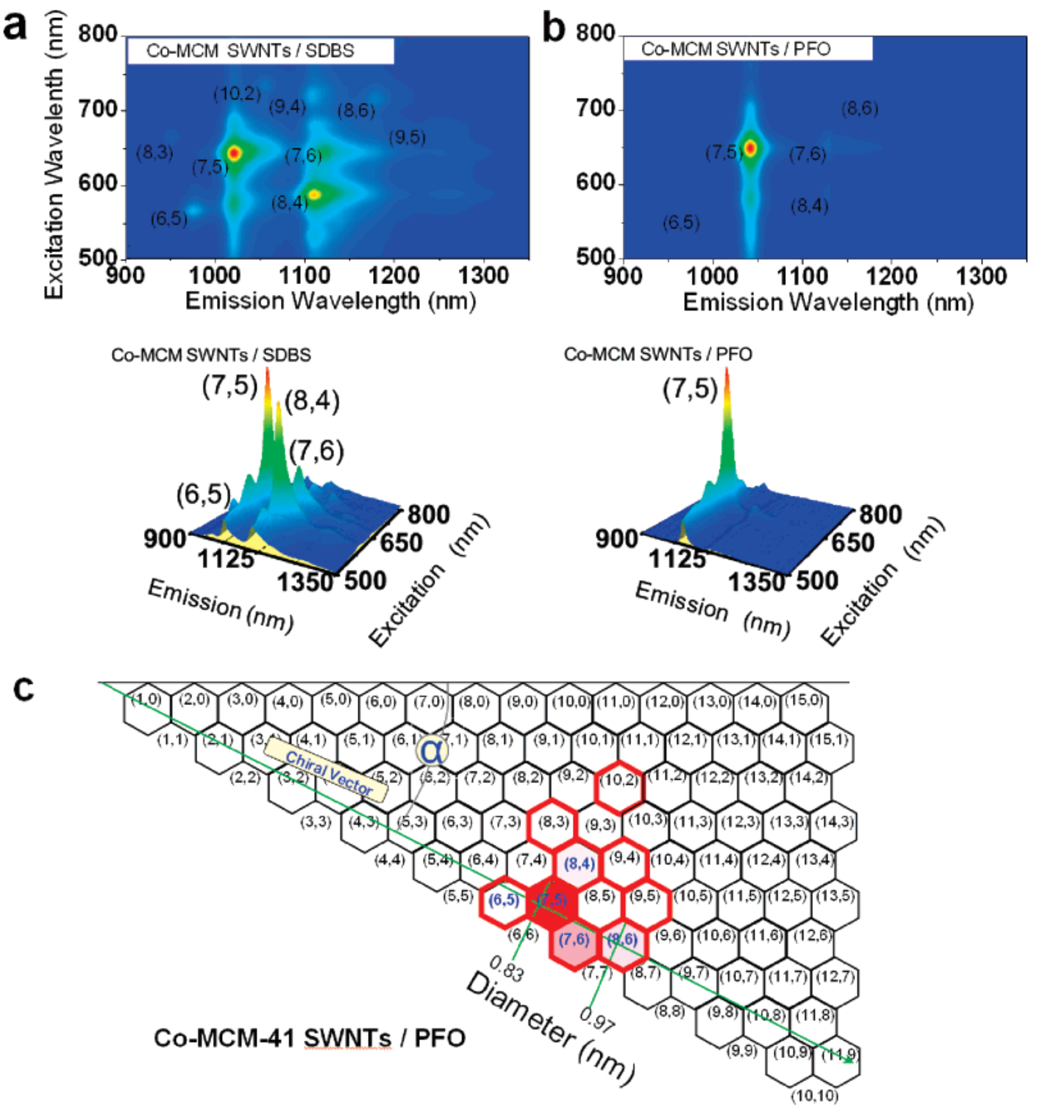

Figure 2. (a,b) PLE mappings for the CoMCM SWNTs dispersed in (a) SDBS/D_2O and in (b) PFO/toluene, respectively. (c) Chirality map showing the wrapping preference of PFO, where the thick and filled hexagons represent the species identified in SDBS/D_2O and PFO/toluene suspension, respectively.

Table 1. Tabulated Values of the Relative Photoluminescence Intensities and Relative Content for Identified Semiconducting Species in CoMCM SWNTs Dispersed in SDBS/D_2O and PFO/toluene Solutions[a]

(n,m)	diameter (nm)	θ (deg)	I_{cal}[b]	diff PL peak intensity[c] (SDBS)	calibrated PL intensity[d] (SDBS)	content (SDBS) (%)	diff PL peak intensity[c] (PFO)	calibrated PL intensity[d] (PFO)	content (PFO) (%)	ratio
(10,2)	0.88	8.9	2.38	22.7	9.55	0.78	0	0.00	0.00	0.00
(8,3)	0.78	15.4	2.13	22.1	10.37	0.85	0	0.00	0.00	0.00
(9,4)	0.92	17.5	0.70	25.3	36.19	2.95	0	0.00	0.00	0.00
(8,4)	0.84	19.1	0.46	234.3	509.30	41.50	5.09	11.07	2.82	0.07
(9,5)	0.97	20.7	0.28	9.7	34.79	2.83	0	0.00	0.00	0.00
(7,5)	0.83	24.5	0.71	260.1	366.34	29.85	219.16	308.68	78.64	2.63
(8,6)	0.97	25.3	0.49	23.8	48.53	3.95	8.5	17.35	4.42	1.12
(6,5)	0.76	27.0	0.67	48.7	72.68	5.92	7.2	10.75	2.74	0.46
(7,6)	0.89	27.5	0.47	65.6	139.53	11.37	21	44.68	11.38	1.00

[a] Ratio indicates the wrapping preference for each species. [b] I_{cal}: calculated PL intensity from Oyama et al.[22] [c] Differential PL intensity: the amplitude of the partial derivative of the PLE map, as suggested by Arnold et al.[14] [d] Calibrated PL intensity: differential PL intensity/I_{cal}.

4.5 mg/L. We have also observed that the sonication time is crucial to the wrapping selectivity. In the beginning of the wrapping process the solution becomes darker with the increasing sonication time, indicating that the wrapping occurs in the early stage. Afterward, the longer sonication period (usually >10 min) results in more SWNT aggregation. From the analysis of optical spectra, we conclude that the extended sonication period results in higher selectivity but

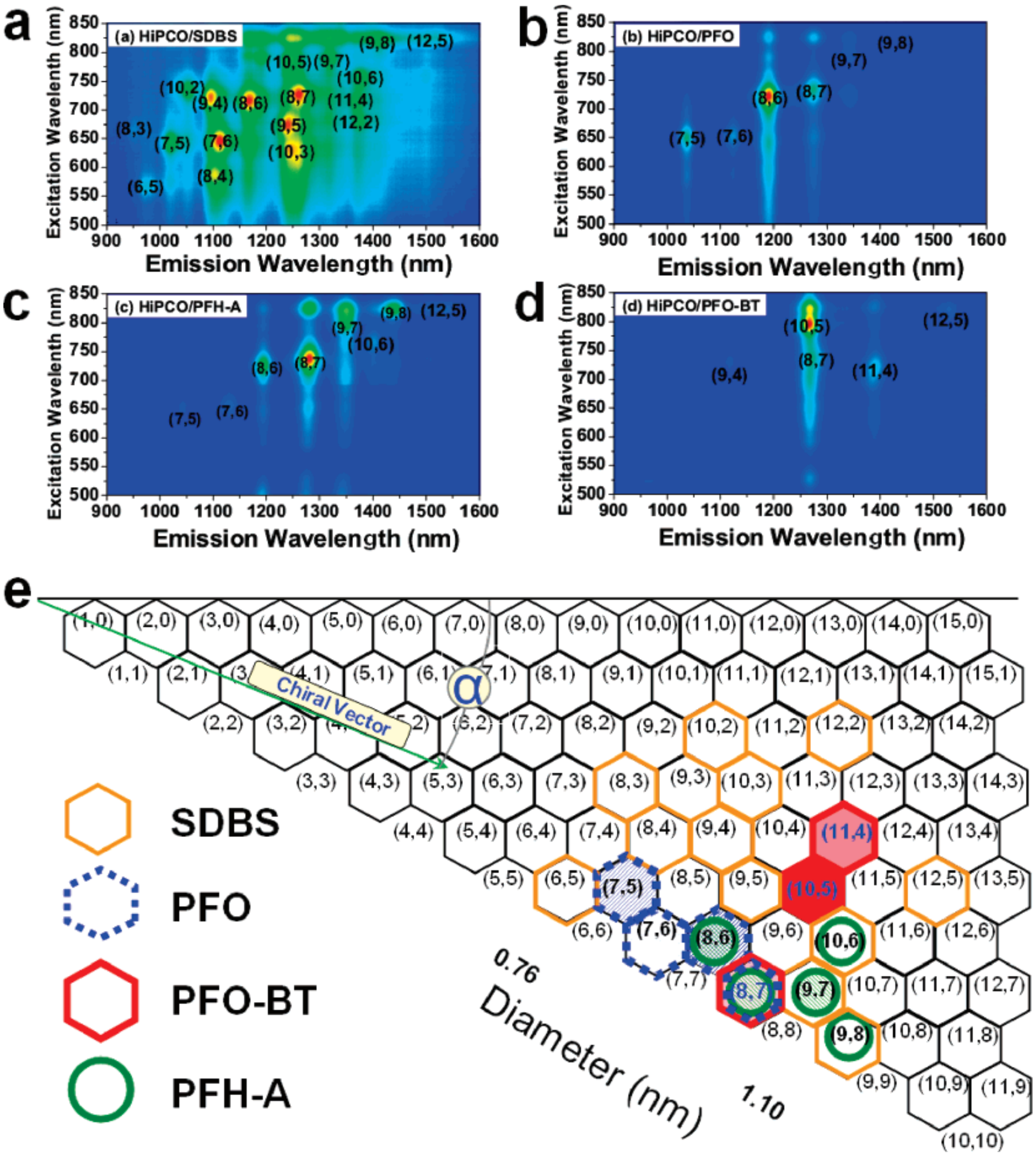

Figure 3. (a−d) PLE mappings for the HiPCO SWNTs dispersed in (a) SDBS/D_2O, (b) PFO/toluene, (c) PFH-A/toluene, and (d) PFO−BT/toluene. (e) Chirality map showing the wrapping preference of PFO, PFH-A, and PFO−BT, where the thick symbols dotted hexagons, hexagons, and circles represent the species identified in PFO, PFO-BT, and PFH-A respectively.

lower efficiency in the wrapping process. We suspect that the extended sonication raises the temperature of the SWNT−polymer−toluene system (or heavily perturbs the system), which then de-wraps and precipitates some of the dispersed SWNTs with lower affinity (lower binding energy) to the polymer. The selectivity is likely due to that the affinity difference in polymer−SWNT for various species is large enough, where the interaction between aromatic rings in SWNT and in polymer could play a dominating role. We believe the wrapping efficiency may be significantly increased by improving the solubility of the polymer and the synthesis of the desired polymers is going on in our lab.

We have also performed the extraction by using several other fluorene-based copolymers such as poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-(1,4-phynylene)] and poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-(bithiophene)] (chemical structures are shown in Supporting Information Figure S3), and no obvious wrapping selectivity was found. We suspect that the aromatic structure in the polymer main chain could selectively interact with different chiral tubes. Our preliminary results in the binding energy between SWNT and polymer (calculated by molecular dynamics) indicate that the aromatic structure in the polymer main chain could dominate the wrapping interaction although the solvent effect is not negligible. More detailed calculation is underway to reveal whether the difference in electron density of SWNT plays a role in the wrapping selectivity.

In summary, high purity of (7,5) SWNTs is obtained by the fluorene-based polymer wrapping process from the narrow-diameter distributed SWNTs produced by the catalyst Co-MCM-41. To further enhance the selectivity and extend this process to other chiral species, the finding in this letter strongly suggests that work on two aspects is crucial. First, various SWNT samples enriched with narrow but distinct chiral species will be most suitable toward the extraction of single species of SWNTs with different chiral structures. Second, more extensive studies on the designs of polymer structure are required to extend or shift the wrapping selectivity toward the SWNTs with a lower chiral angle.

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Supporting Information Available: Values of the relative photoluminescence intensity and relative content for identified semiconducting species HiPCO SWNTs dispersed in SDBS/D2O and PFO/toluene, PFH-A/toluene, PFO-BT/toluene solutions; optical absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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