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One-pot Separation of Highly Enriched (6,5)-Single-walled Carbon Nanotubes Using a Fluorene-based Copolymer

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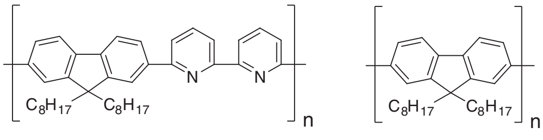
We now describe the finding that a copolymer of 9,9-dioctylfluorenyl-2,7-diyl and bipyridine (BPy) can extract in "one-pot" ≈96–97%-enriched (6,5)-SWNTs in *m*-xylene and *p*-xylene not containing metallic SWNTs, which was revealed by vis–near IR absorption, photoluminescence, and Raman spectroscopies.

Single-walled carbon nanotubes (SWNTs) are potential materials for future electronic devices because of their unique electronic properties.[1] The electronic and optical properties of SWNTs strongly depend on their diameter and chiralities,[2] and depending on their chirality, the SWNTs are metallic or semiconducting.[3] The coexistence of SWNTs with various chiralities in commercially available SWNTs has been an obstacle to their use in fundamental studies as well as large-scale practical applications. It is thus desirable to find a way to separate the semiconducting from metallic tubes.[4]

Recently, two excellent separation methods for single-chirality SWNTs were demonstrated. Arnold et al.[5] reported that a highly polydisperse sample of HiPCO (high pressure carbon monooxide) SWNTs are sorted into ten different enriched (*n*,*m*) fractions by a tailored nonlinear-density-gradient centrifugation (DGU). Furthermore, minor variants of the method allow separation of the minor-image isomers of seven (*n*,*m*) species.[6] Zheng et al.[7] used designed oligo-DNAs to separate twelve (*n*,*m*)-SWNTs each having their own chirality using ion-exchange chromatography (IEX). Although the techniques using the DGU and IEX method have been successfully employed for the separation of SWNTs with different chiralities, the difficulty of scale up limits their applications. We reported a SWNT chirality sorting method using "nanometal sinkers" that adsorb on specific SWNTs, resulting in the separation of nanometal sinker-adsorbed SWNTs and the other SWNTs by density-gradient ultracentrifugation.[8] This method utilizes the difference in the redox potentials of (*n*,*m*)-SWNTs.[9]

Selective SWNT chirality sorting without requiring an additional separation technique, such as IEX and DGC, has been reported. Wei et al. described a multistep extraction of 69%-enriched (6,5)-SWNTs using an aqueous micelle of the co-surfactant of sodium docecyl sulfate and sodium cholate.[10] The selective enrichment of ≈60% (8,4)-SWNTs using a heparin–surfactant mixture extraction was reported by Yan and coworkers.[11] Kim et al.[12] used genomic salmon DNA to enrich 86% of the (6,5)-SNWTs. Papadimitrakopoulos et al.[13] used helical assemblies of the flavin mononucleotide for the extraction of ≈85%-enriched (8,6)-SWNTs. However, for such studies, the extracted SWNTs would contain certain amounts of the metallic SWNTs since the separation of metallic and semiconducting SWNTs using such surfactants and related compounds is quite difficult.



PFO-BPy **PFO**

Figure 1. Chemical structures of PFO–BPy and PFO.

Recently, two groups reported the "one-pot" (sonication only) selective extraction of only semiconducting SWNTs not containing detectable traces of metallic SWNTs from the pristine SWNTs using polyfluorenes (PFOs) as the extracting agent by a simple sonication method followed by ultracentrifugation.[14] The PFOs have a high affinity for small diameter SWNTs and can selectively wrap them with certain chiral angles and dissolve them in solution, in which both the polymer structures and solvent strongly influence the chirality-selective dispersion of the nanotubes.[14c] In particular, poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO, Figure 1) enables the extraction of ≈79%-enriched (7,5)-SWNTs.[14b]

It is still very important to develop a method to obtain highly enriched chirality-selective SWNTs using a simple technique. We now describe the finding that a PFO copolymer (PFO–BPy, Figure 1) composed of long chain-carrying fluorene and bipyridine (BPy) units can extract in one-pot ≈96%-enriched (6,5)-SWNTs not containing metallic SWNTs, which was revealed by vis–near IR (vis/NIR) absorption, photoluminescence (PL), and Raman spectroscopies. Furthermore, we carried out a molecular modeling calculation for the complex of the (6,5)-SWNTs and PFO–BPy. For comparison, we used PFO without the BPy moiety (Figure 1).

Figure 2a shows the vis/NIR absorption spectrum of the CoMoCAT–SWNTs dissolved by the PFO–BPy in toluene, the typical solvent that shows the semiconducting-SWNT-selective extraction using PFOs. We observed a strong peak at 996 nm attributable to the absorption of the (6,5)-SWNTs, in which the background absorption in the NIR region was quite low, which is a typical characteristic of PFO-dissolved SWNT toluene solutions, which is in sharp contrast to many other of dispersants, such as surfactants, aromatic compounds, and polymers, in which we see a significant background absorption in the NIR region.[14] More importantly, almost no absorption appeared in the range of 400–550 nm attributed to metallic SWNTs. This is also an advantage of the PFO dispersants over many other SWNT dispersants.

We examined how the solvent affects the solubilization of the SWNTs using the PFO–BPy. The tested solvents included *o*-xylene, *m*-xylene, *p*-xylene, and THF in addition to toluene, and the results are shown in Figures 2b–2e, in which, except for

Table 1. Calibrated content of SWNT species deduced from PL maps of samples prepared using PFO–BPy and PFO in toluene, *o*-xylene, *m*-xylene, and *p*-xylene

Chiral index (*n*,*m*)	Diameter /nm	Chiral angle /*θ*	Calibrated content/%[16]							
			PFO–Bpy in toluene	PFO–Bpy in *o*-xylene	PFO–Bpy in *m*-xylene	PFO–Bpy in *p*-xylene	PFO in toluene	PFO in *o*-xylene	PFO in *m*-xylene	PFO in *p*-xylene
(6,5)	0.757	27.0	**91.2 ± 1.2**	**87.9 ± 0.4**	**95.7 ± 0.2**	**96.9 ± 0.1**	<0.1	<0.1	<0.1	<0.1
(8,3)	0.782	15.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
(7,5)	0.829	24.5	8.8 ± 1.2	12.1 ± 0.4	4.3 ± 0.2	3.1 ± 0.1	**89.2 ± 0.7**	**88.3 ± 1.3**	**86.9 ± 3.5**	**91.8 ± 1.4**
(8,4)	0.84	19.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
(7,6)	0.895	27.5	<0.1	<0.1	<0.1	<0.1	10.8 ± 0.7	11.7 ± 1.3	13.1 ± 3.5	8.2 ± 1.4

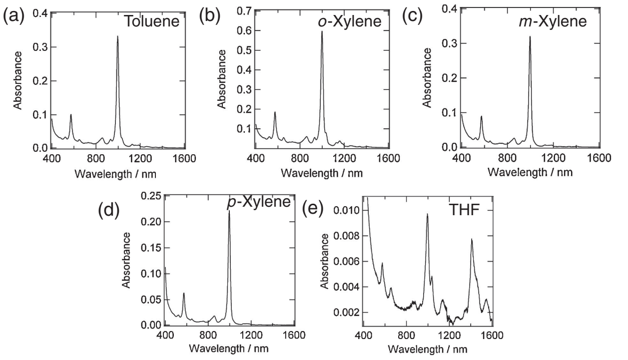


Figure 2. VIS/NIR absorption spectra of dispersed SWNTs using PFO–BPy in toluene (a), *o*-xylene (b), *m*-xylene (c), *p*-xylene (d), and tetrahydrofuran (e).

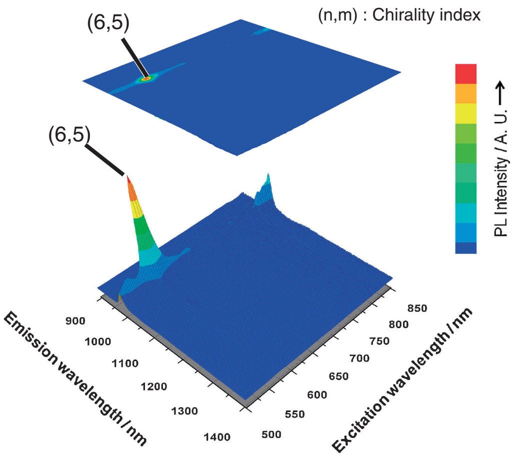


Figure 3. PL maps of the CoMoCAT–SWNTs solubilized by PFO–BPy in *p*-xylene.

THF, we observed a very strong (6,5)-SWNT peak. In sharp contrast, the (6,5)-SWNT selectivity was poor in THF since we observed a clear peak at 1038 nm attributable to the (7,5)-SWNTs together with several peaks at around 1140 nm (Figure 2e), which agrees with those previously reported using PFOs and their derivatives.[14c]

PL spectroscopy is a powerful tool for the determination of the chirality indices of the SWNTs.[5–14] As shown in Figure 3, we only see the (6,5)-SWNTs dissolved by the PFO–BPy in *p*-xylene, and a similar result was obtained in *m*-xylene, while in both toluene and *o*-xylene, we slightly detect the PL from the (7,5)-SWNTs (see Supporting Information, Figure S1).[15] In THF, we see the PL spots from the (6,5)-, (7,5)-, (8,3)-, and (8,4)-SWNTs (see Supporting Information, Figure S1).[15] By using normalized emission intensities, we could calibrate selective extraction values (purity) of the SWNTs, and the results are shown in Table 1. The intrinsic PL efficiency for each chirality of the SWNTs is different, as reported in the literature.[16] The experimental PL intensities were determined from the amplitude of the partial derivative of the PL contour mapping, as suggested by Arnold et al.[5] As is shown in Table 1, the purity of the (6,5)-SWNTs reached ≈96–97% in *m*- and *p*-xylene. *To the best of our knowledge, this is the highest value reported using the one-pot SWNT extraction*. The purity of the (6,5)-SWNTs in toluene and *o*-xylene was ≈88–91%.

As a comparison, CoMoCAT SWNTs were solubilized using PFO in place of PFO–BPy. The purity of the (7,5)-SWNTs in toluene, *o*-xylene, *m*-xylene, and *p*-xylene were ≈89, 88, 87, and 92% (7,5)-SWNTs, respectively (Table 1, see also Figure S2).[15] As described above, PFO has been reported to show a 79%-enriched (7,5)-SWNT-selective extraction.[14] In this study, the purity of the (7,5)-SWNT solubilized by PFO in toluene was higher than that of the reported value, which would be due to high content of the (7,5)-SWNTs in the evaluated CoMoCAT–SWNTs.

It is evident that the introduction of the BPy moiety to the PFO dramatically changes the chiral selectivity, namely, the PFO and PFO–Bpy discriminate the (7,5)-SWNTs and (6,5)-SWNTs, respectively, from the other chiralities of the SWNTs. As can be seen in Table 1, the selectivity of the PFO–BPy (≈97%) was higher than that (≈90%) of the PFO, indicating that the BPy moiety plays an important role in such a high selectivity. The tube diameter and chiral angles of the (6,5)-, (8,3)-, (7,5)-, and (8,4)-SWNTs, which are the major SWNTs contained in the used CoMoCAT–SWNTs, are 0.757, 0.782, 0.829, and 0.840 nm, and 27.00, 15.30, 24.50, and 19.11 degrees, respectively.[17] It is evident that the PFO–BPy recognizes the highest chiral angle nanotubes in the above four SWNTs, and PFO recognizes the second highest chiral angle. The fact that PFO–BPy did not recognizes the (8,3)-SWNTs whose diameter is very close to the (6,5)-SWNTs indicated that the PFO–BPy recognizes not the tube diameter but the chiral angle. A similar tendency is true for the PFO since the tube diameters of the (7,5)- and (8,4)-SWNTs are close. We would like to emphasize that the introduction of the BPy moiety to the PFO dramatically changes the recognizable chiral angle of the SWNTs.

It is known that the solubility of the SWNTs is related to the solvent density and polarity.[14c] In this study, despite the fact that

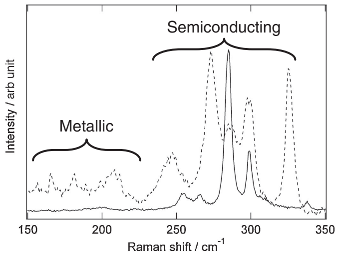


Figure 4. Raman spectra (the RBM frequencies region) of the PFO–BPy-solubilized SWNTs (solid line) and the pristine SWNTs (broken line). Excitation: 633 nm.

the polarity and the density of toluene, *o*-xylene, *m*-xylene, and *p*-xylene were not very different, the purities of the extracted SWNTs by PFO–BPy were somewhat higher in *m*-xylene and *p*-xylene than that in *o*-xylene, while the amount of the solubilized SWNTs was greater in *o*-xylene. The results suggested that the difference in the purity of the (6,5)-SWNTs would be due the difference in the solvent polarity and SWNT-solubility.

To determine whether the extracted SWNTs contain semiconducting- and/or metallic-SWNTs, the Raman spectra (633-nm excitation) of the extracted tubes and the pristine SWNTs were measured (Figure 4). The radial breathing mode (RBM) in the regions of 240–300 and 150–240 cm^{-1} is attributed to the semiconducting and metallic SWNTs, respectively. As can be seen in the figure, for the PFO–BPy-extracted SWNTs, we see clear peaks in the region of 240–300 cm^{-1} and almost no peaks appear in the 150–240 cm^{-1} region, namely, the extracted SWNTs are the semiconducting SWNTs, which well agrees with previous reports using PFOs and their derivatives.[14]

In order to understand the chirality selectivity of the SWNTs, molecular-mechanics simulations using the OPLS2005 force field[18] were carried out between the trimer of 9,9-dioctylfluorenyl-2,7-diyl–BPy and (*n*,*m*)-SWNTs, where $(n,m) = (6,5)$, (7,5), (8,3), and (8,4), and the calculated binding energies (E_{bind})[11] were -1159.7, -1193.1, -1193.5, and -1202.5 kcal mol^{-1} for the trimer and SWNTs having $(n,m) = (6,5)$, (7,5), (8,3), and (8,4), respectively (see Supporting Information, Table S1),[15] which indicates that a rational explanation for the selective extraction of the (6,5)-SWNTs using PFO–BPY using the molecular-mechanics simulations is rather difficult. We also performed a computer simulation to obtain the stable conformation of the trimer with the SWNTs having a chirality index of (6,5), (7,5), (8,3), and (8,4), and the results for the (6,5)-SWNTs are shown in Figure 5 (see Figure S3[15] for the other three chiralities of the SWNTs). For all the four different (*n*,*m*)-SWNTs, the trimer of 9,9-dioctylfluorenyl-2,7-diyl–BPy was found to provide well-packed structures with the SWNTs. Unfortunately, the simplified calculation model is unable to explain the selective interaction between the PFO–BPy and the (6,5)-SWNTs.

In summary, we have succeeded in the selective separation of the (6,5)-SWNTs by a one-pot extraction using PFO–BPy. The purity of the (6,5)-SWNTs estimated from the PL mapping reached 97% and the extracted (6,5)-SWNTs contained only semiconducting SWNTs. The present results indicate that the introduction of the BPy moiety to the PFO polymer dramatically changes the selectivity of the chirality of the SWNTs since the PFO extracted ≈90%-enriched (7,5)-SWNTs. The present study opens a door toward the design of PFO-copolymers that recognize and extract SWNTs with a single chirality.

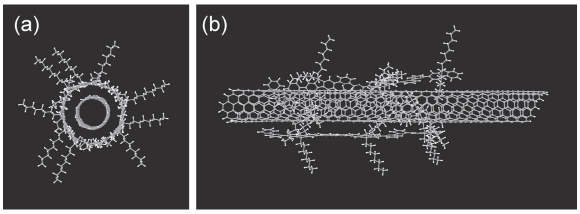


Figure 5. Optimized model structures (top (a) and side (b) views) of the (6,5)-SWNT wrapped with the trimer of 9,9-dioctylfluorenyl-2,7-diyl–BPy.

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