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Rational Concept To Recognize/Extract Single-Walled Carbon Nanotubes with a Specific Chirality

Hiroaki Ozawa,[†] Tsuyohiko Fujigaya,[†] Yasuro Niidome,[†] Naosuke Hotta,[‡] Michiya Fujiki,[‡] and Naotoshi Nakashima[*,†,§]

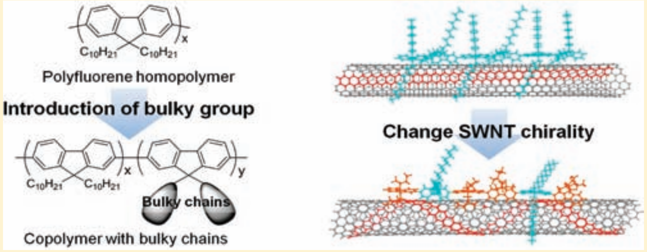
[†]Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan

[‡]Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan

[§]Japan Science and Technology Agency, Core Research of Evolutional Science and Technology, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

S *Supporting Information*

ABSTRACT: Single-walled carbon nanotubes (SWNTs) have remarkable and unique electronic, mechanical, and thermal properties, which are closely related to their chiralities; thus, the chirality-selective recognition/extraction of the SWNTs is one of the central issues in nanotube science. However, any rational materials design enabling one to efficiently extract/solubilize pure SWNT with a desired chirality has yet not been demonstrated. Herein we report that certain chiral polyfluorene copolymers can well-recognize SWNTs with a certain chirality preferentially, leading to solubilization of specific chiral SWNTs. The chiral copolymers were prepared by the Ni^0-catalyzed Yamamoto coupling reaction of 2,7-dibromo-9,9-di-*n*-decylfluorene and 2,7-dibromo-9,9-bis[(*S*)-(+)-2-methylbutyl]fluorene comonomers. The selectivity of the SWNT chirality was mainly determined by the relative fraction of the achiral and chiral side groups. By a molecular mechanics simulation, the cooperative interaction between the fluorene moiety, alkyl side chain, and graphene wall were responsible for the recognition/dissolution ability of SWNT chirality. This is a first example describing *the rational design and synthesis* of *novel* fluorene-based copolymers toward the recognition/extraction of *targeted* (n, m) chirality of the SWNTs.



INTRODUCTION

Much attention has focused on single-walled carbon nanotubes (SWNTs) because of their usefulness for applications in the fields of energy, electronics, and bioscience.[1−8]

However, the coexistence of various chiral SWNTs has interfered with fundamental research and the fabrication of excellent devices. The facile separation of a mixture of SWNTs into specific chirality components has recently attracted great attention. It is desirable to develop a strategy toward the design and synthesis of compounds having a selective SWNT chirality solubilization. Many attempts on this topic have been reported based on the methods using chemical and/or physical modifications. Chemical treatment on surfaces of SWNTs includes octadecyamine-assisted precipitation, oxidation, and selective chemical functionalization by nitronium and halogenations.[9−13] These chemical modifications may, however, alter the physical properties inherent of the SWNTs. As for the physical modification, dielectrophoresis and density-gradient-assisted separation have demonstrated a possibility of nondestructive chirality separation of SWNTs.[14−17] Papadimitrakopoulos and co-workers[18−20] reported that helical assemblies of flavin mononucleotide dissolve SWNTs and have succeeded in the enrichment of (8, 6)SWNT by 85%. Also, Zheng and co-workers successfully purified 12 major single-chirality semiconducting SWNTs using specific oligo-DNAs combined with ion-exchange chromatography.[21,22] We reported a SWNT chirality sorting 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,[23] in which the precise redox potentials of isolated (n, m)SWNTs that we determined very recently[24,25] played a crucial role.

Recently, two research groups reported the semiconductor-enriched SWNTs with the help of achiral polyfluorene homopolymer (**PF**) and its achiral alternating copolymers as the extracting agents.[26−28] Indeed, the purified SWNTs showed excellent electrical properties of a field-effect transistor (FET) device.[29]

Herein we demonstrate a method for the selective recognition and solubilization of selected chirality of (n, m)SWNTs. The study details *the rational design and synthesis* of *novel* copolymers for the specific task of separating/extracting (n, m)SWNTs with a specific chirality, which is a great advance in the design of molecules that dissolve (n, m)SWNTs with a targeted chirality. The approach is to use new π-conjugated **PF**-based copolymers

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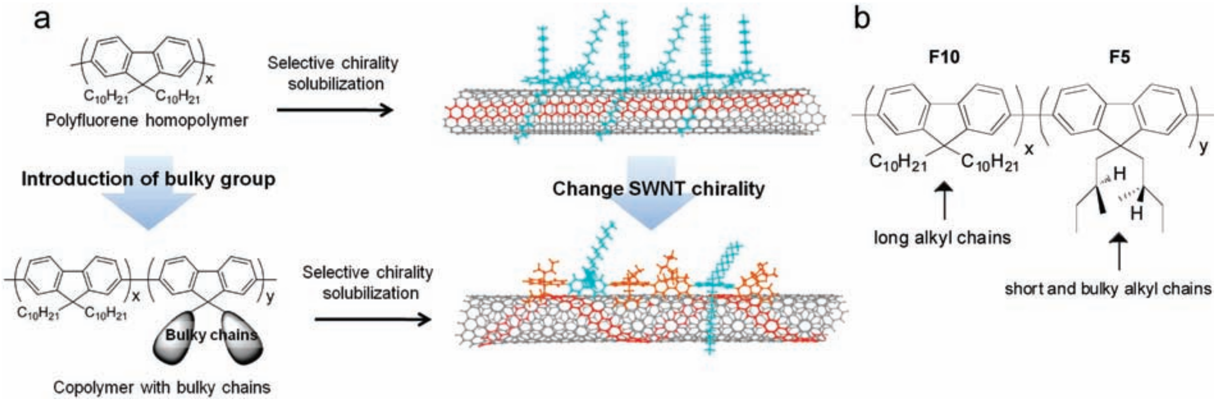


Figure 1. (a) Schematic drawing for the molecular design of compounds (copolymers) that induce the change in SWNT chirality recognition/extraction. (b) Chemical structures of copolymers (copolymer-*x*/*y*) of 9,9-bis[*n*-decyl]fluorene (**F10**) and 9,9-bis[(*S*)-(+)-2-methylbutyl]fluorene (**F5**).

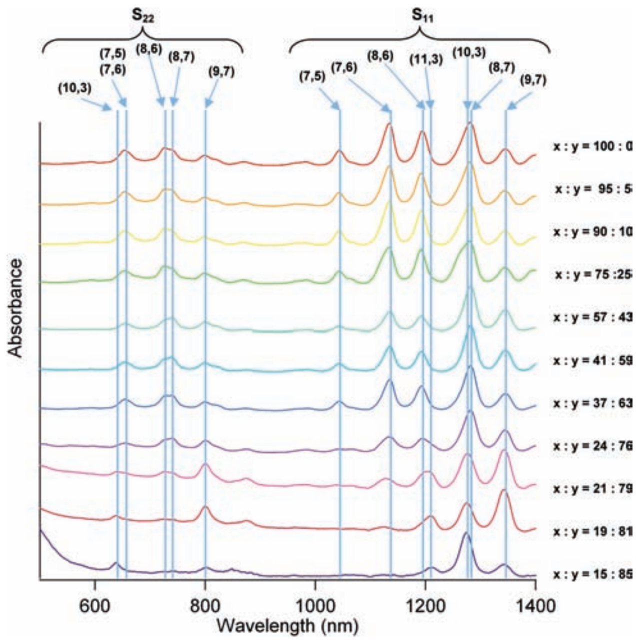


Figure 2. Visible−near-infrared absorption spectra of solubilized SWNTs by copolymer-*x*/*y* with different composition ratios. The copolymerization ratios, *x*:*y*, of **F5** and **F10** are shown on the right side.

carrying achiral and chiral side chains. **PF** homopolymers carrying various achiral side chains are well-known to be useful light-emitting polymeric materials for polymeric LED devices in the range of 400−500 nm. Recently, Nish et al. and Chen et al. found that certain fluorene polymers solubilize selected semiconducting SWNTs in toluene.[26−28] Nicolas et al. used six different **PF** and **PF** derivatives to reveal the polymer structures and solvent effects on the selective dispersion of SWNTs.[28] However, the used compounds are commercially available; therefore, a rational molecular design to selectively recognize and extract SWNTs with a specific chirality is lacking.

Our approach is to use a family of **PF**-based copolymers, composed of a fluorene having two less-bulky, long achiral alkyl side chains to solubilize specific semiconducting (*n*, *m*)SWNTs and a fluorene carrying two bulky, short chiral alkyl side chains. This is important to continuously alter the degree of helical wrapping ability onto the curved surface of the SWNT, as shown in Figure 1a. The fundamental idea is to modulate SWNT chirality recognition/solubilization ability via a steric hindrance of the bulky fluorene unit in the copolymers.

To prove this hypothesis, we synthesized 11 copolymers, copolymer-*x*/*y*, composed of 9,9-bis[*n*-decyl]fluorene (**F10**) and 9,9-bis[(*S*)-(+)-2-methylbutyl]fluorene (**F5**) (Figure 1b). In this paper, we successfully demonstrated that, among a mixture of chiral semiconducting and metallic SWNTs dispersed in toluene, chiral fluorene-based copolymers with the help of appropriate composition of achiral long side chains and bulky short chiral side chains can specifically recognize certain chiralities of semiconducting SWNTs, leading to selective extraction of chiral SWNTs. The present result was also possible to verify by the computer simulations.

EXPERIMENTAL SECTION

The copolymers were synthesized according to the literature.[30] The SWNTs (HiPco, lot R0564) were purchased from Carbon Nanotechnologies, Inc., and used as received. A typical procedure for the SWNT dissolution using the copolymers is as follows: the SWNTs (1 mg) and the copolymer (1 mg) were sonicated in toluene (6 mL) for 1 h, and the dispersion was centrifuged at 10 000*g* for 1 h followed by collection of the supernatant (upper 80%) for the measurements. The vis−near-infrared (NIR) absorption, photoluminescence (PL), and circular dichroism (CD) spectra were measured using a spectrophotometer (JASCO, type V-570), a spectrofluorometer (Horiba-Jobin Yvon, SPEX Fluorolog-3-NIR) equipped with a liquid-nitrogen-cooled InGaAs near-IR detector, and a circular dichroism spectropolarimeter (JASCO, J-820), respectively. The excitation and emission wavelengths were in the range of 500−900 and 900−1300 nm, respectively. The molecular mechanics simulations were carried out using MacroModel (Infocom, version 8.6) with the OPLS-2005 force field. Dielectric constants were kept at 2.3. Minimization on the calculation was carried out using the Polak−Ribiere conjugate gradient with a convergence threshold on the gradient of 0.05 kJ mol^{-1}. Default values were used for all other parameters.

RESULTS AND DISCUSSION

Selective Recognition/Extraction of (*n*, *m*)SWNTs. Polymers (**F10**)*x*(**F5**)*y* were synthesized according to a previously reported method.[30] In this experiment, we used the following homopoymer and 10 copolymers with different copolymerization ratios: (*x*:*y*) = (100:0), (95:5), (90:10), (75:25), (57:43), (41:59), (37:63),

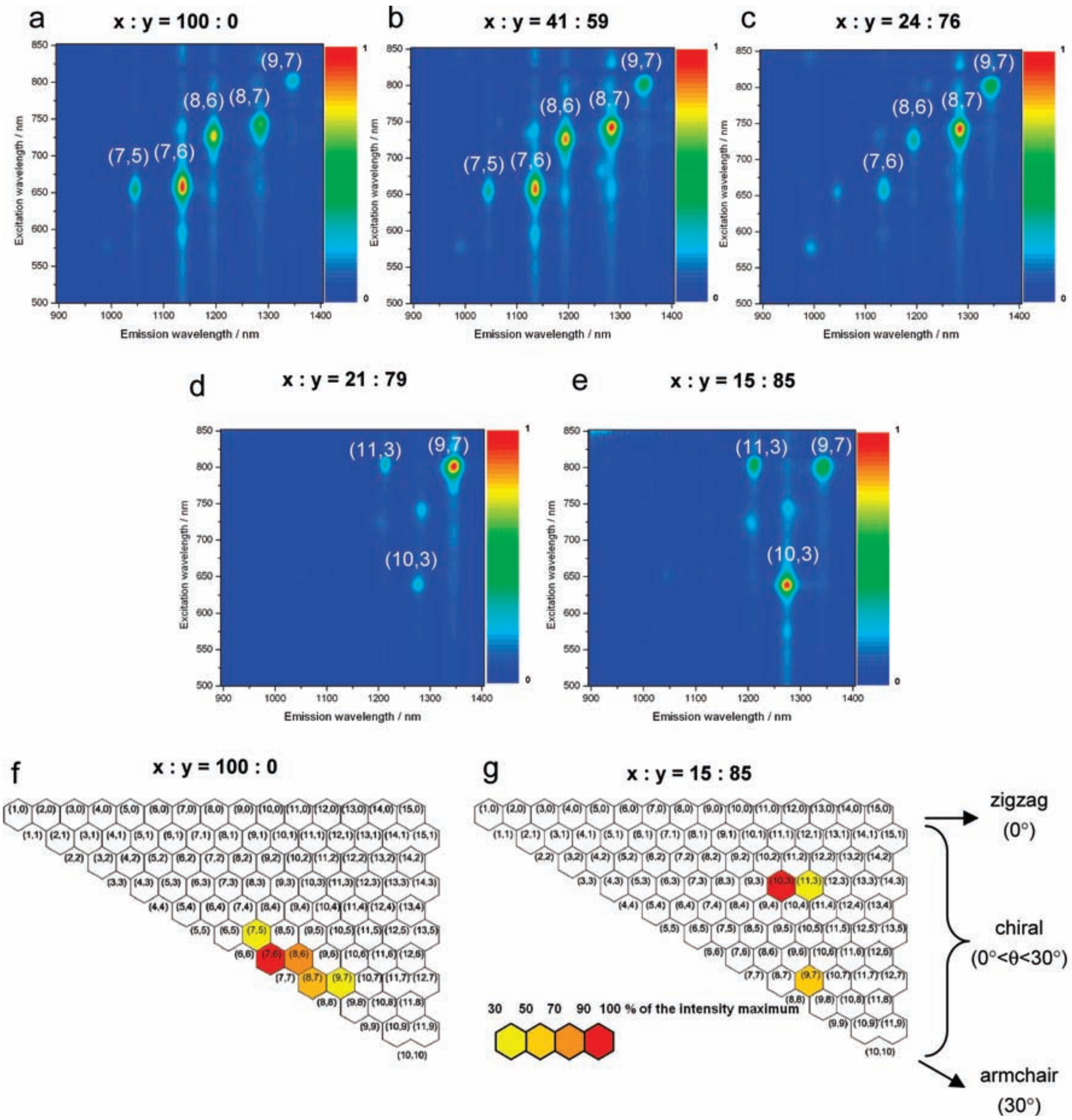


Figure 3. Photoluminescence (PL) and chirality maps of solubilized SWNTs (a−e). PL maps of SWNTs dissolved by copolymers-*x*/*y*. Chirality maps that colored to the SWNTs dissolved by copolymer-100/0 (f) and copolymer-15/85 (g), respectively.

(24:76), (21:79), (19:81), and (15:85), in which *x* and *y* are the composition ratios of **F10** and **F5**, respectively, and their molecular weight and M_w/M_n values were 230 000, 206 000, 607 000, 258 000, 414 000, 260 000, 310 000, 289 000, 242 000, 138 000, 189 000, and 2.44, 3.77, 3.79, 2.16, 3.58, 3.67, 4.19, 2.73, 3.34, 2.90, 3.00, respectively. We used the so-called HiPco-SWNTs, which are the typical SWNTs that have been used widely in the world. The solubilization method is described briefly in the Experimental Section.

The vis−NIR absorption spectra of the solubilized SWNTs using (**F10**)*x*(**F5**)*y* are shown in Figure 2, in which we observe the first (E_{11}) and second (E_{22}) semiconducting bands of the SWNTs having chirality indexes of (7,5), (7,6), (8,6), (11,3), (10,3), (8,7), and (9,7), and almost no metallic band appeared in the range of 400−600 nm, indicating that all the polymers dissolve the semiconducting SWNTs with a high selectively, whose behaviors resemble the results using the previously reported PFOs.[26−28] From the several vis−NIR absorption bands characteristic of chirality of (*n*, *m*)SWNT dissolved in toluene with the help of the polymers (see Figure 2), these vis−NIR intensities strongly depend on both the chirality of the SWNTs and the polymers; however, a further precision evaluation of whether the selective dissolution of the (*n*, *m*)SWNTs is possible is not doable because of the spectral overlapping in the vis−NIR region.

In order to solve this problem, PL from the individually dissolved SWNTs was used to assess the selective solubilization of the above SWNTs with the incorporation of (9,7)SWNTs. Figure 3 shows the 2D-PL mapping and chirality map of the dissolved SWNTs in toluene by five selected copolymers (for other copolymers, see Supporting Information Figure S1), in which we observed a strong SWNT chirality dependence. For instance, the strong PL intensity from the (7,6)SWNTs that appeared in the homopolymer (*x*:*y* = 100:0) became weak with the increase in the composition ratios of the **F5** unit, and disappeared in the copolymer of (*x*:*y*) = 21:79. Although we saw no PL intensity from the (10,3)SWNTs in solutions

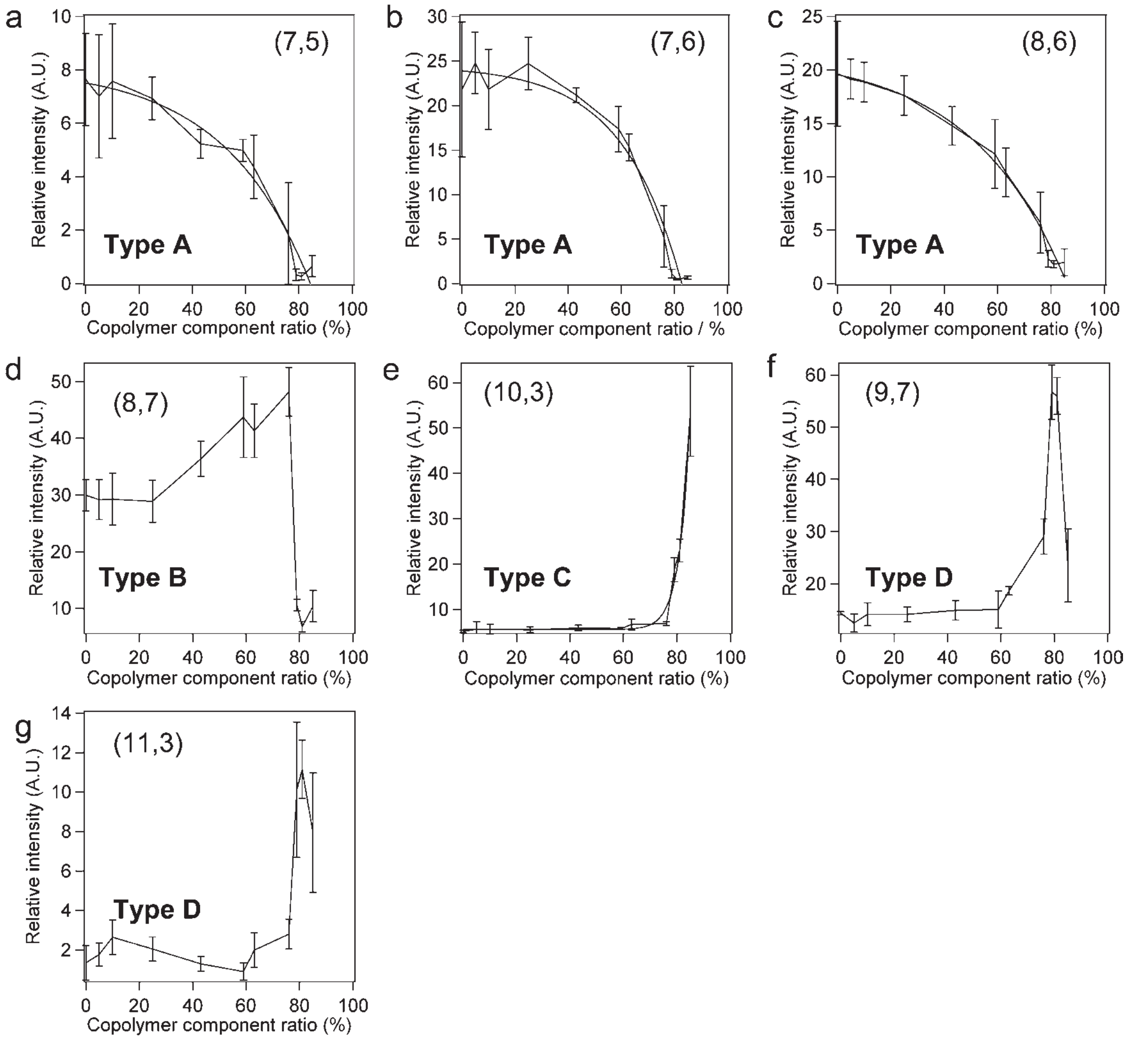


Figure 4. Relationship between PL intensity vs copolymer composition ratios of **F5** (*y* values) (a−g). Relative PL intensities of (7, 5), (7, 6), (8, 6), (8, 7), (9, 7), (10, 3), and (11, 3)SWNTs as a function of copolymerization ratio. These solubilization tendencies were divided into four groups including types A, B, C, and D. The data are averaged from three to six sample sets, with error bars marked.

containing the copolymers with (*x*:*y*) = (100:0), (41:59), and (24:76), the PL intensity from the (10, 3)SWNTs with polymer (15:85) is the strongest.

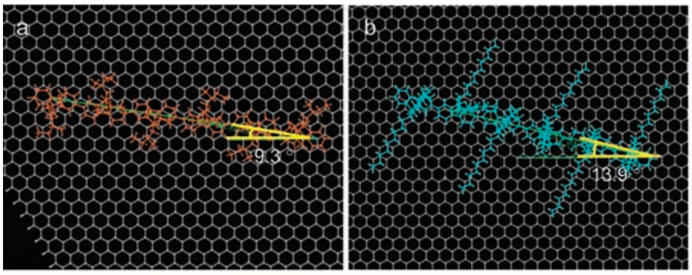
Figure 4 illustrates the normalized PL intensities of the (7, 5), (7, 6), (8, 6), (8, 7), (9, 7), (10, 3), (11, 3)SWNTs as a function of the copolymerization ratios. We used the method reported by Oyama et al.[31] to obtain the normalized PL intensities. The copolymer composition ratio dependence of the PL can be classified into four groups: A, B, C, and D.

The (7, 5), (7, 6), and (8, 6)SWNTs, with diameters less than 1 nm, belong to type A. In this group, the PL intensities gradually decreased with the increase in the ratios of the **F5** unit, followed by an abrupt decrease in PL intensity at **F5** content of over 60%. Type B is composed of the (8, 7)SWNTs with a diameter of 1.032 nm. These SWMTs showed little dependence on **F5** content up to 30%, but the dependence steadily increased over the range of **F5** = 30−76%. However, an especially noteworthy decrease was observed at **F5** = 79%, 81%, and 85%. Type C is composed of the (10,3)SWNTs (diameter = 0.936 nm). As can be seen in Figure 4, the chirality suddenly appeared in the copolymers with **F5** content = 79%, 81%, and 85%, which is the inverse of the (8, 7)SWNT extraction described above. In other words, switching between (8, 7)SWNT extraction and (10, 3)SWNT extraction is made possible by a small change in copolymer composition. The last category is type D, composed of the (9, 7) and (11, 3)SWNTs, with diameters of 1.103 and 1.014 nm, respectively. The behavior of this type is close to that of type C, i.e., the intensities are similar for copolymers with **F5** content up to 76%, but differences appear at **F5** content above 85%.

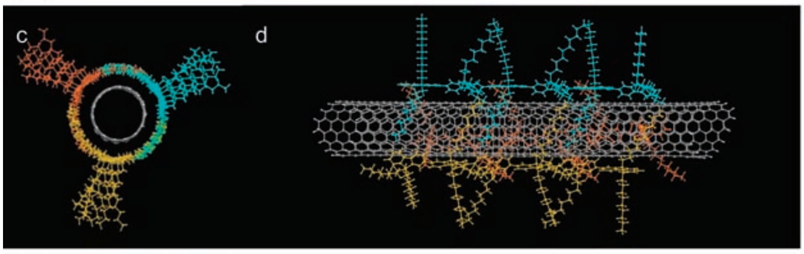
These results confirmed that the copolymers recognize the chiral angles. This is confirmed by the similar behavior of the type C and D SWNTs ((10, 3) and (11, 3)SWNT) with chiral angles of 12.73° and 11.74°, respectively. This behavior is different to that of the type A and B SWNTs with chirality angles greater than 24.50° (see Figure 3, parts f and g).

It was demonstrated that the copolymers do not recognize the tube diameter since the diameter of the type C (10, 3)SWNT (0.936 nm) is close to that of the type A SWNTs ((8, 6)SWNT, diameter = 0.966 nm) and the (11, 3)SWNTs' diameter (1.014 nm) is close the (8, 7)SWNT's diameter (1.032 nm).

We have measured the CD spectra of the synthesized copolymers (see Supporting Information Figure S2), which would be informative on helical conformation of the copolymers, and found that the CD intensity increased almost linearly with the



(8,7)-SWNT with **F10** hexamers



(10,3) -SWNT with **F5** hexamers

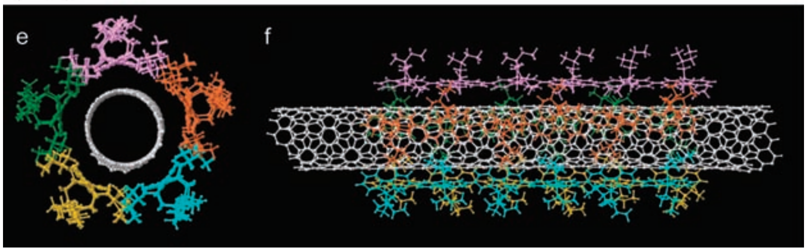


Figure 5. Optimized model structures of **F5** (a) and **F10** hexamers (b) on graphene sheets. Model structures showing top and side views of two (8, 7)SWNT with **F10** hexamers (c and d) and (10, 3)SWNT and **F5** hexamers (e and f).

increase in the composition ratios of the **F5** moiety. This behavior is quite different from the phenomena shown in Figure 4, indicating that the chiral conformation of the copolymers might not be significant for the dramatic composition ratio dependence in the recognition/extraction of the (n, m)SWNTs with a specific chirality.

Molecular Mechanics Simulations. In order to understand the importance of the chiral angle of the SWNTs in chirality recognition, molecular mechanics simulations using the OPLS2005 force field[32] were carried out for hexamers of **F10** and **F5.** Figure 5, parts a and b, shows the optimized structures of the **F5** and **F10** hexamers on graphene sheets, in which the angles between the long axis of the **F5** and **F10** hexamers and the graphene sheet were 9.3° and 13.9°, respectively. The optimized structures were strongly influenced by the structures of the alkyl chains.

The calculated binding energies (E_{bind})[33] between the hexamers **F5** and **F10** with the (7, 5), (7, 6), (8, 6), (11, 3), (10, 3), (8, 7), and (9, 7)SWNTs are given in Table 1. The values of E_{bind} between these seven different (n, m)SWNTs and the **F5** hexamer are not so different, being in the range of -316.4 to -328.6 kcal mol^{-1}. Contrarily, the values of E_{bind} between the (n, m)SWNTs and the **F10** hexamer are very different, being in the range of -415.0 to -384.9 kcal mol^{-1}, suggesting a greater chirality dependence rather than the **F5** case. This situation is similar to the case of the (8, 6) and (10, 3)SWNTs, which have 0.966 and 0.936 nm diameters, respectively. The stability of the (8, 6)-SWNTs presumably originates from the cooperativity by efficiently adding-up weak CH/π interactions with a minimal mismatch in lattice parameters between the plural C—H bonds of long alkyl chains and the fused hexagons of the chirally curved graphene surface (as illustrated in Supporting Information Figure S3). Although our molecular mechanics simulations might require further rigorous conditions, the present result should provide a possible explanation of the reason why the (10, 3)SWNTs were not efficiently extracted by the **F10**-rich copolymers.

Although the (9, 7)SWNTs and **F10** gave the highest E_{bind} value, the extraction of SWNTs with the **F10**-rich copolymers was not very efficient. At present, a dramatic increase followed by a decrease in the selective extraction of the (9, 7) and (11, 3)SWNTs at around 80% **F5** content is difficult to explain by this calculation. Multiple factors, including the copolymer structures and the solubility of the nanotube/copolymer hybrids, would be expected to affect the selective extraction.

In order to explain the results shown above, we performed a computer simulation to seek the most stable conformations of the hexamers onto curved surface of chiral CNT. We focused on the (8, 7) and (10, 3)SWNTs because these were well-extracted by the specialized copolymers. The calculation revealed that the combination of three **F10** hexamers with the (8, 7)SWNTs and five **F5** hexamers with the (10, 3)-SWNTs provide the most stable conformations. A schematic drawing for the result is shown in Figure 5, parts c (top view) and d (side view), and Figure 5, parts e (top view) and f (side view), respectively, who are in well-packed structures. A further calculation of the stable conformations between other chiral SWNTs and hexamers (see Supporting Information Figure S4) showed that the **F5** hexamers can form densely packed structures with (7, 5) and (7, 6)SWNTs. This calculation,

Table 1. Calculated Potential and Binding Energies between a SWNT with an **F5** or **F10** Hexamer

(n,m)	diameter (nm)	potential energy of SWNT E_{SWNT} (kcal mol^{-1})	potential energy of **F5** E_{F5} (kcal mol^{-1})	total potential energy ($E_{F5} + E_{SWNT}$) (kcal mol^{-1})	potential energy of complex E_{comp} (kcal mol^{-1})	binding energy $E_{bind} = E_{comp} - (E_{F5} + E_{SWNT})$ (kcal mol^{-1})
(7, 5)	0.829	36938.3	859.7	37798.0	37481.0	−317.0
(7, 6)	0.895	37491.3	859.7	38351.0	38028.4	−322.6
(10, 3)	0.936	33384.9	859.7	34244.6	33928.2	−316.4
(8, 6)	0.966	38015.2	859.7	38874.9	38548.7	−326.1
(11, 3)	1.014	36905.2	859.7	37764.8	37443.3	−322.5
(8, 7)	1.032	38750.6	859.7	39610.3	39281.8	−328.6
(9, 7)	1.103	39481.4	859.7	40341.1	40008.5	−332.6

(n,m)	diameter (nm)	potential energy of SWNT E_{SWNT} (kcal mol^{-1})	potential energy of **F10** E_{F10} (kcal mol^{-1})	total potential energy ($E_{F10} + E_{SWNT}$) (kcal mol^{-1})	potential energy of complex E_{comp} (kcal mol^{-1})	binding energy $E_{bind} = E_{comp} - (E_{F10} + E_{SWNT})$ (kcal mol^{-1})
(7, 5)	0.829	36938.3	499.6	37437.9	37050.0	−388.0
(7, 6)	0.895	37491.3	499.6	37990.9	37584.1	−406.8
(10, 3)	0.936	33384.9	499.6	33884.5	33499.6	−384.9
(8, 6)	0.966	38015.2	499.6	38514.8	38099.9	−414.9
(11, 3)	1.014	36905.2	499.6	37404.8	36986.4	−418.3
(8, 7)	1.032	38750.6	499.6	39250.2	38828.2	−422.0
(9, 7)	1.103	39481.4	499.6	39981.0	39548.5	−432.5

however, did not agree with the actual experiment. Alternatively, although a combination between the (11, 3)SWNTs and the **F5** hexamers did not provide such a densely packed structure, the copolymer with the **F5** content of 85% selectively extracted the (11, 3)SWNT. At the moment, all these simulations led to the conclusion that the oversimplified calculations between the hexamers and the nanotubes cannot well explain the reason why certain chiral fluorene copolymers can selectively recognize/extract the CNT with a certain chirality dominantly. To predict a more general CNT chirality selection rule by chiral polymers, a further rigorous computer simulation based on more careful conditions with plural factors remains an unsolved issue.

CONCLUSIONS

In summary, we have presented a rational concept of how to recognize SWNT chiralities and solubilize them in a solvent. The method is to use fluorene-based copolymers composed of 9,9-bis[*n*-alkyl]fluorene and 9,9-bis[(*S*)-(+)-2-methylbutyl]fluorene units. We have discovered a regulated SWNT chirality recognition/dissolution by changing the copolymer composition ratios due to the SWNT chiral angle recognition by the copolymers. A molecular mechanics simulation partially explained this behavior based on binding energies and close packing. The present study opens a door toward the design of molecules that recognize and extract SWNTs with a selected or single chirality.

ASSOCIATED CONTENT

Supporting Information. PL mapping of solubilized SWNT with copolymers, magnified images of model structures, and model structures showing top views of seven nanotubes encased with two types of hexamers. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

nakashima-tcm@mail.cstm.kyushu-u.ac.jp

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