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Different Chiral Selective Recognition/Extraction of (*n*,*m*)Single-walled Carbon Nanotubes Using Copolymers Carrying a Carbazole or Fluorene Moiety

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We describe the finding that copolymers having a long-double chain carbazole or fluorene group connected to benzothiadiazole with thiophene linkers show a different chiral selective (*n*,*m*)single-walled carbon nanotube (SWNT) solubilization behavior which was revealed by 2D photoluminescence and vis–near IR spectroscopies. We also carried out molecular mechanical simulations to understand the difference in the chiral selective solubilization behavior.

Nanocarbon composite materials have attracted much attention due to their potential applications in the fields such as energy, electronics, and sensing.[1–4] In particular, nanocomposites of single-walled carbon nanotubes (SWNTs) and polymers are expected to be candidates for future organic electroluminescence (EL) and solar cell materials.[5–9] However, the coexistence of various chiral SWNTs has interfered with fundamental research and the fabrication of electronic devices. The facile separation of a mixture of SWNTs into specific chiral components has recently attracted significant attention. Two groups have recently reported the selective separation of SWNTs using polyfluorene (PFO) as the extracting agent.[10] Very recently, we reported that certain chiral PFO copolymers can well recognize an SWNT with a certain preferential chirality, leading to solubilization of specific chiral SWNTs.[11,12]

Polycarbazole and fluorene have been extensively studied as a component of light-emitting diodes (LEDs) and photovoltaic devices.[13] Here we describe selective SWNT solubilization using copolymers of long-double chain carbazole and thiophene/benzothiadiazole (copolymer **1**) and of long-double chain fluorene and thiophene/benzothiadiazole (copolymer **2**) (Figure 1). Carbazole (or fluorene) connected to benzothiadiazole with thiophene linkers are known to be electron-rich units for intramolecular charge transfer in LED materials,[14] and the copolymers **1** and **2** are promising high-performance LED and solar cell materials; therefore, the combination of copolymers **1** or **2** and the SWNTs are of interest.[14,15] Very recently, Lemasson et al. reported SWNT solubilization behavior using *N*-decylpolycarbazole and a dioctylpolyfluorene polymer, in which they sonicated ca. 50 mg of the polymers and ca. 1 mg SWNTs followed by density gradient ultracentrifugation (DGU) to obtain individually dissolved SWNTs.[16] They reported that the *N*-decylpolycarbazole preferentially extracted seven (*n*,*m*)SWNTs with $(n - m) \geq 2$ in toluene, which is complementary to the (*n*,*m*)SWNTs which are preferentially dispersed by the dioctylpolyfluorene polymer. Although the SWNT solubilization is different, they used the single-chain (C10) polycarbazole and double-chain (2C8) polyfluorene. It is known that SWNT solubilization has a chemical structure dependence based on the solubilizers used. In this study, we used both double (2C8)-chain copolymers as the dispersants, both of which show a rather high SWNT solubilization potential and compared the chiral selective SWNT dissolution for samples prepared by simple sonication and ultracentrifugation without the DGU procedure.

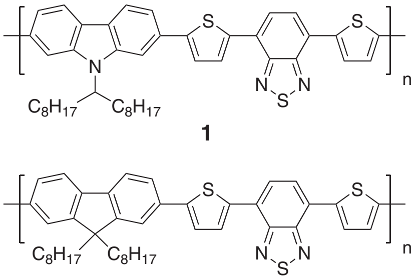

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Figure 1. Chemical structures of copolymers **1** and **2**.

The polycarbazole derivative **1** and polyfluorene derivative **2** were synthesized according to a previously reported method[14,17] and characterized by FT-IR (Perkin-Elmer, Spectrum 65 FT-IR), NMR (Bruker, AV300M spectrometer), and GPC (JASCO, MD-2015 Plus with TOSHO, TSK-GEL α-3000 and TSK-GEL α-M). A typical procedure for the preparation of the SWNT solutions using copolymers **1** and **2** is as follows. The HiPco-SWNTs (1 mg, Unidym) were added to a toluene solution (6 mL) of the copolymer (2 mg) and then sonicated for 1 h using a bath sonicator followed by centrifugation at 10000 *g* for 1 h. After removing the excess polymers by filtration using a poly(tetrafluoroethylene) membrane (pore size; 0.1 µm), the filtered solid was resolubilized in toluene using the sonicator for 0.5 h. The amount of each 1 mg copolymer was found to well solubilize the SWNTs, which was used for the characterization described below.

The UV–vis–near IR absorption spectra (JASCO, V-570) of the obtained SWNT solutions using copolymers **1** and **2** are shown in Figures 2a and 2b, in which sharp S_{11} and S_{22} bands of the SWNTs are observed in the range of 1000–1500 and 600–800 nm, respectively, which resembles the spectra of the SWNTs dissolved in a PFO toluene solution.[10] In Figure 2a (also see Supporting Information (SI),[18] Figure S1),[18] we observed a red shift in copolymer **1** by 30 nm in the visible region due to the complexation with the SWNTs. For copolymer **2**, the red shift

Table 1. Calibrated content of the SWNT species deduced from the PL mappings of the samples prepared using copolymers **1** and **2** in toluene

Chiral index of SWNTs (*n*,*m*)	I_{cal}[a]	PL peak intensity (arb unit)		Calibrated PL intensity (arb unit)		Calibrated content/%[22]	
		by Copolymer **1** in toluene	by Copolymer **2** in toluene	by Copolymer **1** in toluene	by Copolymer **2** in toluene	by Copolymer **1** in toluene	by Copolymer **2** in toluene
(6,5)	0.67	1169	124.5	1745	185.8	4.7	5.3
(7,5)	0.71	1546	140.1	2177	197.3	5.8	5.7
(7,6)	0.47	3145	269.1	6691	572.6	17.9	16.5
(8,6)	0.49	3221	324.6	6573	662.4	17.6	19.0
(8,7)	0.3	2436	558.0	8120	1860.0	21.7	53.5
(9,4)	0.7	2232	not detected	3188	not detected	8.5	not detected
(9,5)	0.28	2501	not detected	8932	not detected	23.9	not detected

[a] I_{cal}; calculated PL intensity from Oyama et al.[22]

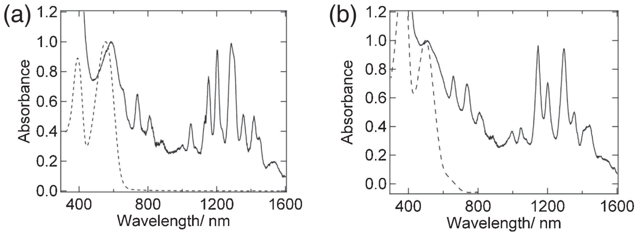

Figure 2. (a) UV–vis–NIR absorption of copolymer **1** (broken line) and solubilized SWNTs by **1** (solid line) in toluene. (b) UV–vis–NIR absorption spectra of copolymer **2** (broken line) and solubilized SWNTs by **2** (solid line) in toluene.

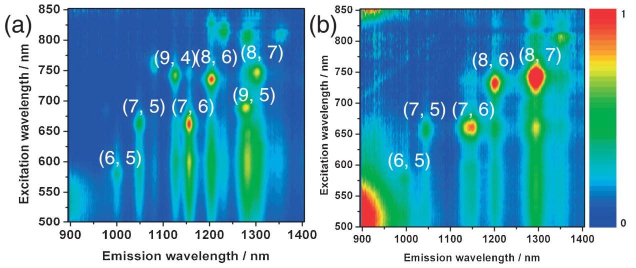

Figure 3. 2D-PL mappings of the copolymer **1**/SWNTs (a) and copolymer **2**/SWNTs (b) in toluene.

was much smaller (Figure 2b and SI, Figure S1).[18] It is known that the shift may arise from an increased effective conjugation length of π-conjugated polymers by the interaction with the SWNT surfaces.[19]

Photoluminescence (PL) spectroscopy is a powerful tool for the determination of the chirality indices of the SWNTs.[10] Figure 3 shows 2D-PL mapping (HORIBA SPEX Fluorolog-3-NIR spectrofluorometer equipped with a liquid-nitrogen-cooled InGaAs near-IR detector), in which we see the (6,5)-, (7,5)-, (7,6)-, (8,6)-, (8,7)-, (9,4)-, and (9,5)SWNTs dissolved by copolymer **1** in toluene and the (6,5)-, (7,5)-, (7,6)-, (8,6)-, and (8,7)SWNTs extracted by copolymer **2** in toluene. Our carbazole copolymer **1** did not show "(*n*,*m*)SWNTs with $(n - m) \geq 2$" dependence. The lower section of the PL maps shows a luminescence from the same SWNTs, but in this case with excitation at shorter wavelengths. This spectral range does not correspond to any electronic transitions in the nanotubes. It can be seen that emission occurs via energy transfer from the copolymer and other SWNTs.[20,21] We obtained the relative content of the identified semiconducting species from PL for both copolymers **1** and **2** wrapped SWNTs. The intrinsic PL efficiency for each chirality of the tubes is different, as reported in the literature; therefore, we calculated the relative content of each SWNT based on the calibrated PL intensity using a method reported by Saito et al.[22] The content of the (6,5)-, (7,5)-, (7,6)-, (8,6)-, (8,7)-, (9,4)-, and (9,5)SWNTs using **1** and **2** were ca. 4.7, 5.8, 17.9, 17.6, 21.7, 8.5, and 23.9% and ca. 5.3, 5.7, 16.5, 19.0, 53.5, <0.1, and <0.1%, respectively (Table 1). We recognized that the (8,7)- and (9,5)SWNTs, and (8,7)SWNTs are enriched in copolymers **1** and **2**, respectively. It is evident that the difference in the fluorene units and carbazole units changes the chiral selectivity, namely, the copolymer **1** having the carbazole units recognizes the middle chiral angle SWNTs, such as the (9,4)- and (9,5)SWNTs.

In order to understand the chirality-selective SWNT recognition/extraction, molecular mechanics simulations using the OPLS2005 force field[23] were carried out between the trimer of *N*-9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole), 2,7-(9,9-dioctylfluorene)-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole), and the (*n*,*m*)SWNTs, where (*n*,*m*) = (7,6), (9,4), (8,6), and (9,5). All calculations were optimized in MacroModel (version 8.6) with an OPLS-2005 force field. Energy minimization was carried out using the Polak–Ribiere conjugate gradient (PRCG) with a convergence threshold on the gradient of 0.05 kJ mol^{-1}. The default values were used for all the other parameters.

The diameters of the SWNTs with the chiral indices (7,6) and (9,4) are close, namely, 0.895 and 0.916 nm, respectively, while their chiral angles (27.5 and 17.5° for the (7,6)- and (9,4)SWNTs, respectively) are quite different. The calculated binding energies (E_{bind})[24] between copolymer **1** (trimer) and the (7,6)- and (9,4)SWNTs were −467.7 and −461.9 kcal mol^{-1}, respectively, and those between copolymer **2** (trimer) and the (7,6)- and (9,4)SWNTs were −465.4, and −447.5 kcal mol^{-1}, respectively (see SI, Table S1).[18] It was found that the E_{bind} values between the (7,6)- and (9,4)SWNTs with copolymer **1** (trimer) are not very different, whereas the binding between the (9,4)SWNT with the copolymer **2** (trimer) is weaker than that between the (7,6)SWNT with **2** (trimer). This calculation agrees

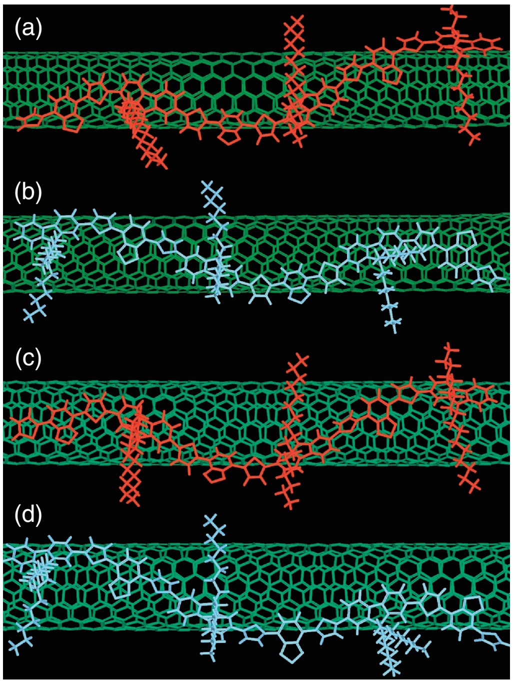

Figure 4. Model structures (side views) showing the interactions of the (7,6)SWNT with the trimers of **1** (a) and **2** (b) and of the (8,6)SWNT with the trimers of **1** (c) and **2** (d).

with the PL results. For the interactions between the (8,6)- and (9,5)SWNTs and copolymer **1** (trimer) and copolymer **2** (trimer), a similar explanation is possible, and the calculation also agrees with the PL results. All these results suggest that the SWNT chiral angle recognition by the copolymers is important for the selective extraction.

We also performed a computer simulation to obtain a stable conformation of the copolymers **1** and **2** (both trimers) with the SWNTs having a chiral index of (7,6), (9,4), (8,6), or (9,5) (Figure 4 and SI, Figure S2[18]). The conformation of copolymer **2** (trimer) on the (7,6)SWNT is distorted compared to that of the copolymer **1** (trimer) on the (7,6)SWNT, suggesting a decrease in the effective conjugation length, which agrees with the observed red shift in the absorption spectra described above. This tendency is similar to the case of the (8,6)SWNTs (Figure 4).

In conclusion, we described different chiral selective recognition/extractions of the SWNTs using copolymers **1** and **2** having double long-chain carbazole and fluorene functional groups, respectively. By using molecular mechanics simulations, we revealed the mechanism of the difference in the chiral selective SWNT recognition/extraction. The study is useful to understand the mechanisms of the chiral selective extraction of the SWNTs, and the obtained composites of copolymers **1** and **2** and the semiconducting SWNTs are of interest for applications in electronic devices as well as solar cells and LED devices.

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