

Selective Extraction of Semiconducting Single-Wall Carbon Nanotubes by Poly(9,9-dioctylfluorene-*alt*-pyridine) for 1.5 μm Emission

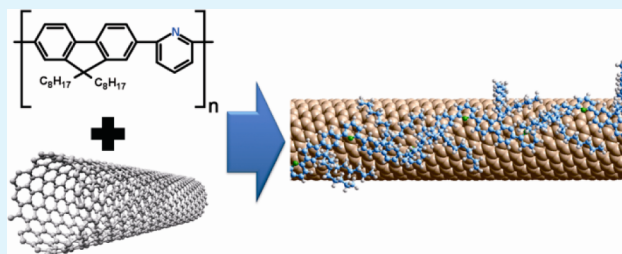
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S Supporting Information

ABSTRACT: For applications in standard optical devices, single-wall carbon nanotubes (SWCNTs) exhibiting emissions near 1500 nm are potentially feasible because silicon semiconductors efficiently transmit the light in this region. However, techniques to extract such semiconducting SWCNTs have not been reported thus far. In this study, using poly(9,9-dioctylfluorene-*alt*-pyridine) (PFOPy) as a dispersant in organic solvent, we succeeded in selectively dispersing SWCNTs which show near-infrared fluorescence around 1500 nm. On the basis of optical absorption and photoluminescence excitation spectroscopy, we revealed that the outstanding tube-structure preference of PFOPy can be interpreted by a characteristic “wavy” conformation of PFOPy on the tube wall.

KEYWORDS: selective extraction, fluorene-pyridine copolymer, single-wall carbon nanotubes, near-infrared emissions, polymer conformation, polymer backbone



Near-infrared (NIR) light-emitting organic materials, such as polymer nanocrystals with tunable (from 1000 to 1300 nm) emissions¹ and trivalent rare-earth (RE) complexes with 1500-nm emissions,^{2,3} have drawn great attention for the development of silicon-integrated optoelectronic devices. In particular, the spectral region from 1500 to 1600 nm is known as the third telecommunications window (c-band) and is crucial for NIR photonic devices because of the absorbance minimum of silica optical fiber, which leads to low optical attenuation.⁴ Normally, organic molecules containing no RE ions show NIR fluorescence shorter than ~ 1000 nm.¹ Therefore, it has been difficult to achieve NIR fluorescence beyond 1500 nm with organic compounds that lack RE ions.

On the other hand, single-wall carbon nanotubes (SWCNTs) not only are flexible and lightweight but also exhibit a variety of electronic properties: metallic or semiconducting features associated with the tube structures (tube diameter and chiral angle).⁵ In particular, semiconducting SWCNTs are promising materials for photonic devices for telecommunication⁶ because of their NIR fluorescence, for which wavelengths can be changed by SWCNT tube structures identified by chiral indices (n,m).⁷ Moreover, for small-diameter tubes (<1.2 nm), semiconducting SWCNTs with specific tube structures can be extracted from as-produced SWCNTs, including a variety of tube structures, by several extraction techniques: for example, polymer wrappings with rigid polymers such as polyfluorene (PFO)^{8,9} and polycarbazole,¹⁰ DNA wrapping,¹¹ density-gradient ultracentrifugation,^{12,13} and gel chromatography.¹⁴ In particular, the polymer wrapping method leads not only to the enrichment of specific semiconducting SWCNTs but also to

low backgrounds in the absorption spectrum. These features contribute to the high photoluminescence quantum yields ($\sim 1\%$) in the polymer-extracted SWCNTs,¹⁵ and are especially useful for the fabrication of photoelectronic devices.¹⁶

However, to the best of our knowledge, rigid polymers which can selectively extract specific semiconducting SWCNTs showing NIR fluorescence at the telecommunication wavelengths from 1500 to 1600 nm have not been reported so far. For example, when specific semiconducting SWCNTs with narrow diameter distributions are extracted via PFO wrapping, the emission wavelengths of the extracted SWCNTs are below ~ 1350 nm.^{8,9} In addition, large-diameter SWCNTs extracted via fluorene-benzothiadiazole copolymer (F8BT) wrapping also are somewhat unsuitable for applications in optical communications because the extracted SWCNTs exhibit a somewhat wider diameter distribution, and consequently, exhibit NIR emissions in a wide range, over 1520–1900 nm.¹⁷ Furthermore, F8BT shows the chiral-angle selectivity not only for large-diameter tubes¹⁷ but also for small diameter tubes;^{8,9} the chiral-angle selectivity observed in a wide range of tube diameters hinders the narrowing of a tube-diameter distribution. Therefore, polymers with the ability to selectively extract specific SWCNTs with a narrow diameter distribution leading to NIR fluorescence close to 1500 nm are highly desirable for uniform

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fluorescence properties of SWCNTs in the telecommunications window.

In the present work, we succeeded in extracting semi-conducting SWCNTs showing 1500 nm emission with a narrow diameter distribution using poly(9,9-dioctylfluorene-*alt*-pyridine) (PFOPy) as a dispersing agent in toluene. The photoluminescence excitation (PLE) map of the PFOPy-extracted SWCNTs showed clearly intense and sharp emissions of a few (n,m) species occurring in the vicinity of 1500 nm. The diameter distribution width in the PFOPy-extracted SWCNTs was approximately 0.15 nm, significantly narrower compared to F8BT-extracted SWCNTs (0.25 nm distribution width).¹⁷ The ability to narrow the diameter distribution can be interpreted by the characteristic conformation of PFOPy, proposed on the basis of molecular mechanics simulations.

Figure 1 shows the absorption spectrum of PFOPy-extracted SWCNTs, together with a reference spectrum of SWCNTs

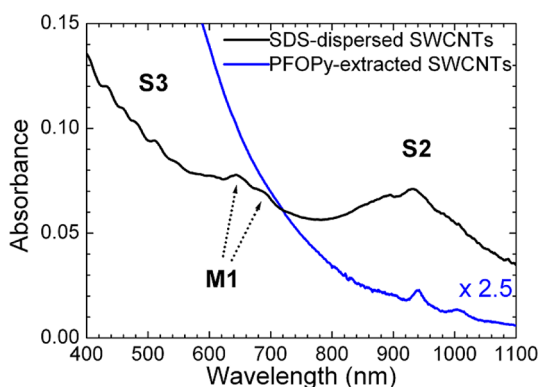


Figure 1. Absorption spectra of PFOPy-extracted SWCNTs in toluene and SDS-dispersed SWCNTs in D₂O. For the relatively higher signal-to-noise ratio, a PFOPy-extracted SWCNT solution concentrated via partial solvent evaporation was used; the intense signal of the solution at shorter wavelengths (<700 nm) is mainly due to PFOPy concentrated by the evaporation. For the preparation of these solutions, PLV-SWCNTs with $d_t = 1.0\text{--}1.4$ nm were used as an initial material. Absorption bands indicated by S2, S3, and M1 arise from the second and third optical transitions of semiconducting tubes and the first optical transitions of metallic tubes, respectively.

dispersed by sodium dodecyl sulfate (SDS) in D₂O. Here, large-diameter SWCNTs synthesized by the pulsed-laser vaporization (PLV) method were used as an initial material¹⁸ with diameters (d_t) in the range 1.0–1.4 nm. In the absorption spectrum of SDS-dispersed SWCNTs, the absorption bands due to the second (S2) and third (S3) optical transitions of semiconducting SWCNTs were clearly observed in the wavelength ranges of $\lambda = 750\text{--}1100$ nm and $\lambda < 600$ nm, respectively, which was consistent with the previous report for PLV-SWCNTs.¹⁹ In addition, two peaks centered at about 645 and 690 nm also appeared between the S2 and the S3 transition bands, which can be assigned to the absorptions (M1) of metallic SWCNTs.

In contrast, the absorption spectrum of PFOPy-wrapped SWCNTs clearly showed the absence of the M1 absorptions, implying the preferential extraction of semiconducting SWCNTs via PFOPy wrapping. Moreover, in contrast to the broad S2 absorption peak of SDS-dispersed SWCNTs, a structured S2 band was observed, which suggests the preference of PFOPy for specific semiconducting (n,m) tubes. Such a structured absorption band appears to be a common feature in

large-diameter SWCNTs extracted selectively via polymer wrapping.¹⁷

The selectivity of PFOPy in extracting specific semiconducting (n,m) tubes was obviously revealed with the PLE maps of the SWCNT solutions. The PLE maps of SDS-dispersed and PFOPy-extracted SWCNTs are shown in panels a and b in Figure 2, respectively, which were obtained with

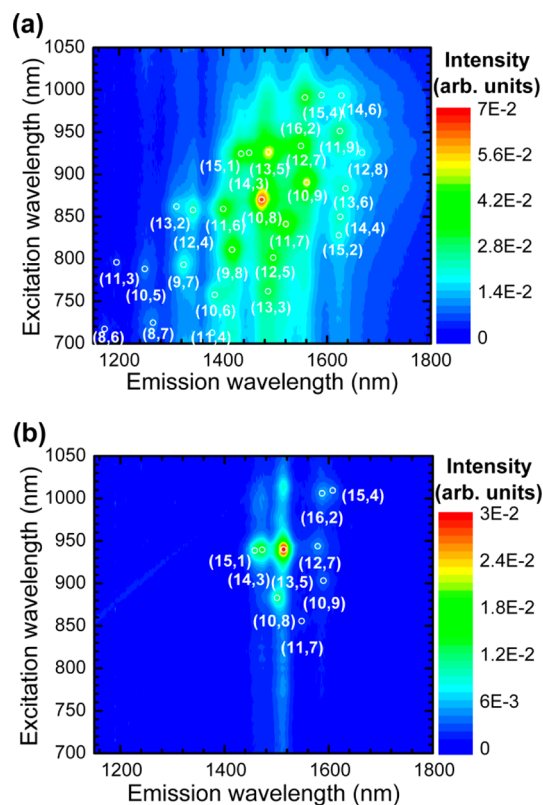


Figure 2. PLE maps excited at visible-NIR wavelengths for (a) SDS-dispersed SWCNTs in D₂O and (b) PFOPy-extracted SWCNTs in toluene.

visible-NIR wavelength excitations in the range from 700 to 1050 nm. These excitations lead to emissions from SWCNTs excited through the S2 optical transition. Each emission in the PLE maps can be assigned to different chiral indices (n,m) using predictions of emission peaks from empirical functions by Weisman and Bachilo.²⁰ In SDS-dispersed SWCNTs, various emission peaks indicating a variety of (n,m) species can be observed because of the almost negligible chirality preference of SDS, as shown in Figure 2a.

In contrast, the PLE map of PFOPy-extracted SWCNTs in Figure 2b was remarkably different from that of SDS-dispersed SWCNTs. Intense and sharp emissions of a few (n,m) species were observed, indicating the remarkable chirality preference of PFOPy. From the PLE map, in particular, (13,5), (14,3), and (10,8) SWCNTs were found to be extracted, exhibiting fluorescence around 1500 nm. The line widths of the emissions were significantly narrow, implying that the SWCNTs were well debundled in toluene via PFOPy wrapping. For example, when the PL spectra (in units of energy) containing emissions of different (n,m) SWCNT species were deconvoluted with Lorentzian line shapes, the line width of the emissions from the PFOPy-extracted (13,5) SWCNTs was 12 meV, comparable to that of isolated SWCNTs,^{21,22} whereas SDS-

dispersed (13,5) SWCNTs showed broad emissions with a line width of 27 meV.

Meanwhile the PL peaks at the emission wavelength around 1680 nm should be strongly suppressed because of the strong absorption peak of toluene.¹⁷ For example, the PL peak of (12, 8) SWCNTs almost disappears in the PL map of poly(9,9-didodecylfluorene) (PFD)-extracted SWCNTs even though the tubes are apparently contained in the solution (Figure S6).¹⁷ However, such effect is not significant for the other SWCNTs. Indeed the PL peaks of (11,9), (14,6), (13,8), and (11,10) SWCNTs are still observable even in the vicinity of 1680 nm (see Figure S6 in the Supporting Information). Therefore, it is reasonable that the fewer PL peaks in Figure 2b suggest the narrower distribution of the extracted SWCNTs by PFOPy. The sharp peaks of the S2 transition (Figure 1) in contrast to the broader spectrum of PFD-extracted SWCNTs¹⁷ also support the PL results.

In comparison with large-diameter SWCNTs extracted by F8BT,¹⁷ the narrow diameter distribution of PFOPy-extracted SWCNTs can be observed as a noticeable difference (see Figure S3 in the Supporting Information). Figure 3 shows

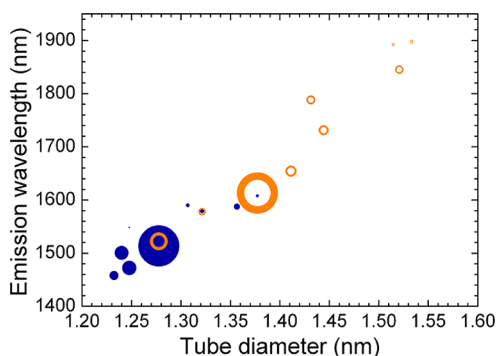


Figure 3. Emission wavelengths of PL peaks in PFOPy-extracted SWCNTs (blue circles) with those of F8BT-extracted ones (orange circles)¹⁷ as a function of tube diameter. The relative emission intensities in SWCNTs extracted by each polymer were transformed into the size of plotted circles.

emission wavelengths of PL peaks of PFOPy-extracted SWCNTs with tube diameters, in which the observed PL intensities are denoted as the size of the circles. Here we simply use the PL intensities to estimate the (n, m) distribution because the PL quantum efficiencies of the tubes are unknown. Nevertheless, it is still very useful to investigate the population changes of (n, m) tubes.¹⁰ Obviously, PFOPy-extracted SWCNTs with the narrower diameter distribution compared to the F8BT-extracted SWCNTs exhibit emissions near 1500 nm. The diameters of PFOPy-extracted SWCNTs were distributed over 1.23–1.38 nm, which was much narrower compared to F8BT-extracted SWCNTs (1.28–1.53 nm)¹⁷ (see the Experimental Section in the Supporting Information for the detail of each initial SWCNT material used for two different polymer wrappings).

It was reported that fluorene-based polymers used for selective extraction of specific SWCNTs show the planarization of the polymer backbones in particular solvents, e.g., toluene.²³ The concentrated solution of PFOPy also shows characteristic absorption and excitation spectra suggesting the planarization of PFOPy backbones (see Figure S2 in the Supporting Information). The planarization could lead to relatively strong interaction between specific SWCNTs and PFOPy similar to

the case of PFO and F8BT achieving selective extraction of specific SWCNTs (see the Supporting Information for details).^{8,9,17}

To investigate the reason for the extremely narrow diameter distribution, we simulated the configurations between a SWCNT and a fluorene-pyridine oligomer using a molecular mechanics approach (Figure 4).^{8,10,24,25} A (13,5) tube was

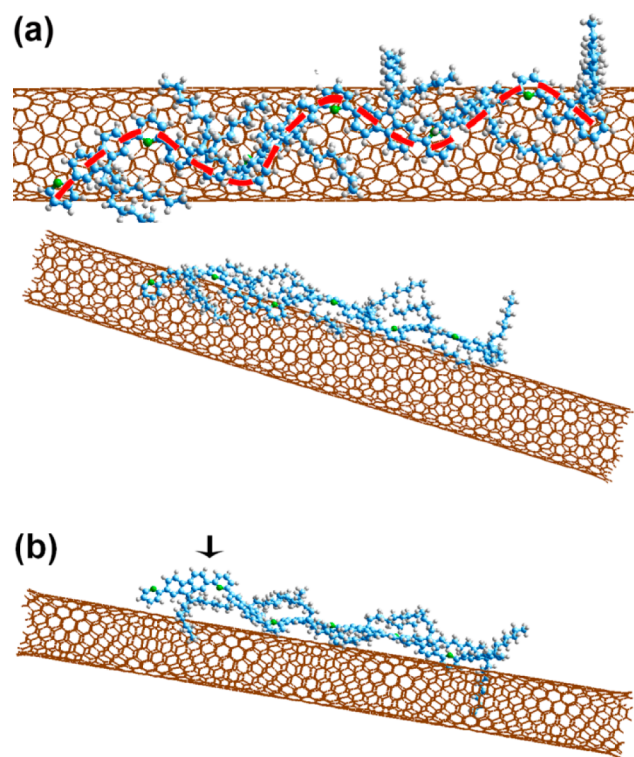


Figure 4. Simulated configurations between a fluorene-pyridine oligomer and each SWCNT: (a) the (13,5) nanotube (top panel: top view, and bottom panel: side view) and (b) the (9,7) nanotube. The zigzag shape of the oligomer backbone is depicted with a red dashed line. The part of the oligomer backbone which deviates from the surface of the (9,7) tube is indicated by an arrow.

selected for the simulation because conformational matching between the (13,5) tube and PFOPy was expected on the basis of the preference of PFOPy for the intermediate chiral angles and large diameters (1.2–1.3 nm) (see Figure S3 in the Supporting Information). For comparison, a (9,7) tube with a relative small diameter (1.10 nm) and a large chiral (25.9°) was also selected. Normally, fluorene-based polymers such as PFO and F8BT and carbazole-based polymers wrap individual SWCNTs with the polymer backbones aligned along the tube axis or forming long-pitch helices,^{8,10,24,25} resulting in the selective extraction of specific semiconducting SWCNTs. In contrast, polymers with no selectivity for specific semiconducting SWCNTs, e.g., poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-phenylene)], have somewhat flexible backbones, which are coil-like chains, helically wrapping individual SWCNTs.²⁵ For PFOPy, the oligomer was found to have a zigzag-shaped backbone (i.e., wavelike chain) as shown in Figure 4a, where a (13,5) tube with a 1.28 nm diameter was used for simulation.

This simulated oligomer conformation was obviously different from rod-like and coil-like chains.^{8,10,25} Wavelike chains presumably interact strongly with the walls of SWCNTs with

diameters close to 1.28 nm, consequently leading to the narrow diameter distribution of the PFOPy-extracted SWCNTs. For example, in (13,5) tubes, which can be extracted via PFOPy wrapping, the π - π interactions of the SWCNT walls with the zigzag-shaped backbones are expected to be stronger than those in small-diameter tubes, such as (9,7) tubes with diameters of 1.10 nm. In fact, although (9,7) tubes can be extracted by PFO wrapping,^{8,9} PFOPy preferentially extracts (13,5) tubes instead of (9,7) tubes, as can be seen from Figure 2b. In the case of (9,7) tubes, a mismatch between the wall of the SWCNT and the aromatic structure of PFOPy will occur because of the PFOPy structure which extends perpendicularly to the tube axis, i.e., the zigzag-shaped backbone. According to the simulated configuration between a (9,7) SWCNT and the oligomer, a part of the fluorene-pyridine oligomer was found to deviate from the wall of the (9,7) tube, as shown in Figure 4b. This speculation, based on the morphology of the oligomer obtained by the simulations, is consistent with the result showing the high sensitivity of PFOPy to tube diameter (Figure 3): PFOPy has the ability to narrow the diameter distribution of SWCNTs.

The abilities to not only narrow the diameter distribution but also extract specific semiconducting SWCNTs with diameters close to 1.28 nm are valuable for investigating photophysical properties which depend on SWCNT tube structures. Thus far, either PFO or F8BT has been used for studies on a variety of the properties of specific (*n,m*) SWCNTs.^{15,26–29} However, the studies were restricted to small-diameter tubes of less than 1.2 nm because of the lack of polymers for selective extraction of specific large-diameter SWCNTs with a narrow diameter distribution. The selectivity of PFOPy for specific large-diameter tubes will be useful not only for applications to silicon-integrated photonic devices operating at the telecommunication wavelengths^{2,3} but also for the investigation of photophysical properties defined by tube structure in large-diameter SWCNTs.

In conclusion, we have succeeded in the selective extraction of specific large-diameter SWCNTs showing obvious NIR fluorescence in the vicinity of 1500 nm, using PFOPy. In addition, the diameter distribution of the extracted SWCNTs was significantly narrower than that of F8BT-extracted large-diameter SWCNTs. The ability to narrow the diameter distribution can be interpreted as being due to the characteristic conformation of PFOPy on the basis of simulations of configuration between a SWCNT and a fluorene-pyridine oligomer.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, planarization of PFOPy backbone in toluene, chirality preferences of PFOPy and F8BT, characteristic emissions indicating exciplex formation, chemical structure of PFOPy, optical characterization of PFOPy solutions, and PL intensities of SDS-dispersed and PFOPy-extracted (*n,m*) SWCNTs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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