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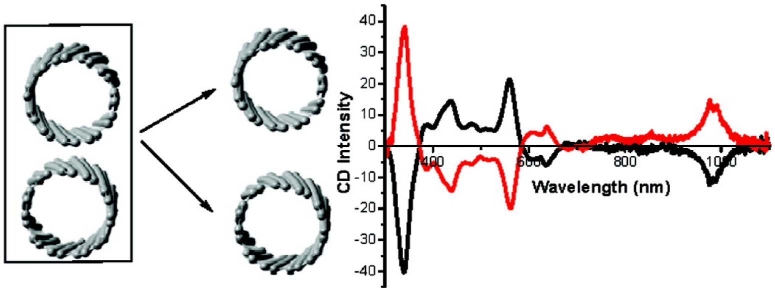

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Improved Optical Enrichment of SWNTs through Extraction with Chiral Nanotweezers of 2,6-Pyridylene-Bridged Diporphyrins

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Abstract: Chiral single-walled carbon nanotubes (SWNTs) have left- and right-handed helical structures (*M* and *P*, respectively, according to the IUPAC nomenclature). In this report, optically active SWNTs were obtained through preferential extraction of (*M*)- or (*P*)-SWNTs with 2,6-pyridylene-bridged chiral diporphyrins **1**. In the circular dichroism (CD) spectra, the SWNTs extracted with **1** exhibit much larger intensity than those extracted with 1,3-phenylene-bridged chiral diporphyrins **2**, indicating an improved chiral discrimination ability of **1**. In particular, (6,5)-SWNTs display the most intensified CD signals among the SWNTs extracted with **1**. In addition, the SWNT extraction ability of **1** has been shown to be considerably enhanced in comparison to **2**. These improved discrimination and extraction abilities of **1** are attributed to the formation of its more stable SWNT complex. Computer-calculated energy minimized structures for **1**:(6,5)-SWNT complexes show that (*R*)- and (*S*)-**1** form complexes preferentially with (*M*)- and (*P*)-(6,5)-SWNTs, respectively. These calculations also predict that the **1**:(6,5)-SWNT complex is $\sim$1.6 kcal mol^{-1} more stable than the corresponding complex of **2**, accounting for the improved abilities of **1** in the chiral discrimination and extraction.

Introduction

Single-walled carbon nanotubes (SWNTs) have a cylindrical structure wrapping a graphene sheet. The structure is defined by a roll-up vector $\boldsymbol{C}_h$, given by two unit vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$; $\boldsymbol{C}_h = n\boldsymbol{a}_1 + m\boldsymbol{a}_2$, where *n* and *m* are integers and designated as the index (*n*, *m*).[1,2] It can be easily imagined that SWNTs with similar diameters include many kinds of the indices, making structural control of SWNTs very difficult. In addition, one kind of chiral SWNTs has a pair of handedness, left-handed (*M*) and right-handed (*P*) forms, making the situation more complicated.[3]

In view of their fundamental studies and technological applications,[4] SWNTs with specific structure are of great demand, as the electrical and optical properties of carbon nanotubes are largely dependent on their structures.[5] Since SWNTs were first prepared in 1993,[6,7] much effort has been directed toward selective synthesis and separation of SWNTs with limited structures or specific properties.[8−22] However, optical activity originating from carbon nanotubes themselves has been elusive until our recent result.[23,24] In this work, optically active SWNTs

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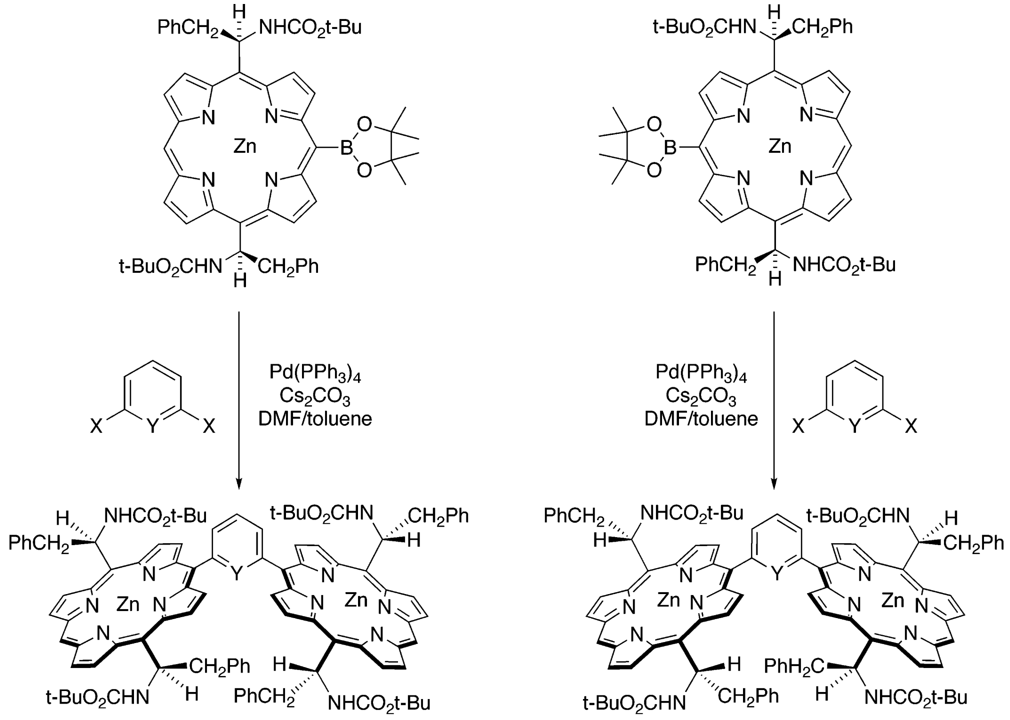
Scheme 1. Synthesis of Chiral Diporphyrin **1** and **2** through Suzuki−Miyaura Coupling Reaction



R **1**: X = Br, Y = N *S*
2: X = I, Y = CH

were obtained for the first time through molecular recognition of the helical isomers of SWNTs by 1,3-phenylene-bridged chiral diporphyrins **2**.[24] An advantage of this host−guest strategy lies in the flexibility in molecular design of the diporphyrins, which may allow the exploration of nanotweezers with improved ability in structural discrimination of carbon nanotubes. Such a modification study will give us a conceptual guidance for the design of tweezers. Here, we designed and synthesized 2,6-pyridylene-bridged chiral diporphyrin **1**, which has a smaller dihedral angle (93.8°) of the two porphyrin rings compared to **2** (111.2°). Such a subtle structural change in a tweezers molecule is found to lead to considerable improvements in extraction and chiral discrimination abilities of SWNTs.

Results and Discussion

Terminology of Helical Structures in Carbon Nanotubes. As Strano pointed out in one article,[25] a systematic nomenclature is desired to define the structures of carbon nanotubes. In particular, the usage of "chirality or chiral" is confusing; "chirality" is defined in the field of organic chemistry as "the geometric property of a rigid object of being non-superposable on its mirror image".[26] Tweezers **1** and **2**, and all of the SWNTs other than zigzag and armchair, are chiral and can have pairs of the mirror-images. According to the IUPAC nomenclature,[26] the stereochemistry of the tweezers and the SWNTs should be designated as *R* and *S*, and *M* and *P*, respectively. In this paper, we follow the IUPAC terminology;[26] that is, the left- and right-handed structures of carbon nanotubes are referred to as *M* and *P*,[27] instead of the various expressions used so far, *LH* and *RH*,[24] *r* and *l*,[28] *L* and *R*,[3] (n_1, n_2) and (n_2, n_1),[29] and *AL* and *AR*,[1] on the basis of the definition of *AL* and *AR*.[1] The term "chiral" is used exclusively in the meaning of having the non-superposable property on its mirror image throughout this paper.[26] In addition, we intend to avoid the usage of "chirality" and "chiral vector" for the meaning of the (n, m) index in carbon nanotubes. The latter is designated as roll-up vector according to the Strano's proposal.[25] Accordingly, "chiral angle" is referred to as roll-up angle under the same definition.[1,2]

Synthesis of Chiral Nanotweezers. Chiral diporphyrin nanotweezers **1** and **2** were prepared via Suzuki−Miyaura coupling reactions of the corresponding boronated (*R*)- or (*S*)-monoporphyrin with 2,6-dibromopyridine and 1,3-diiodobenzene, respectively, as shown in Scheme 1.[24] The chiral monoporphyrins were prepared from 2,2′-dipyrrylmethane and (*R*)- or (*S*)-phenylalaninal, according to the reported procedure.[24]

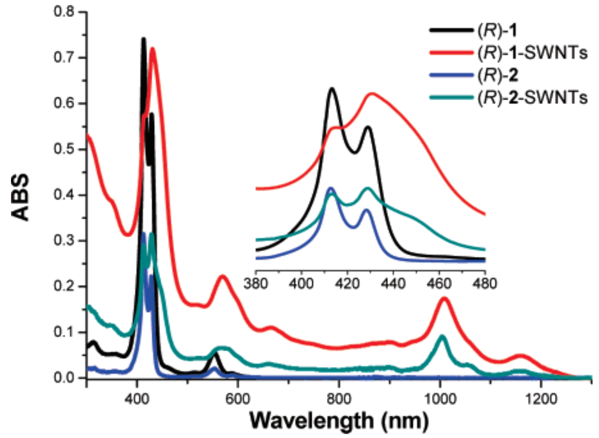


Figure 1. UV−vis-NIR of (*R*)-**1**, (*R*)-**1**:SWNTs, (*R*)-**2**, and (*R*)-**2**:SWNTs in MeOH. Inset: expansion of the spectra in the region of 380−480 nm.

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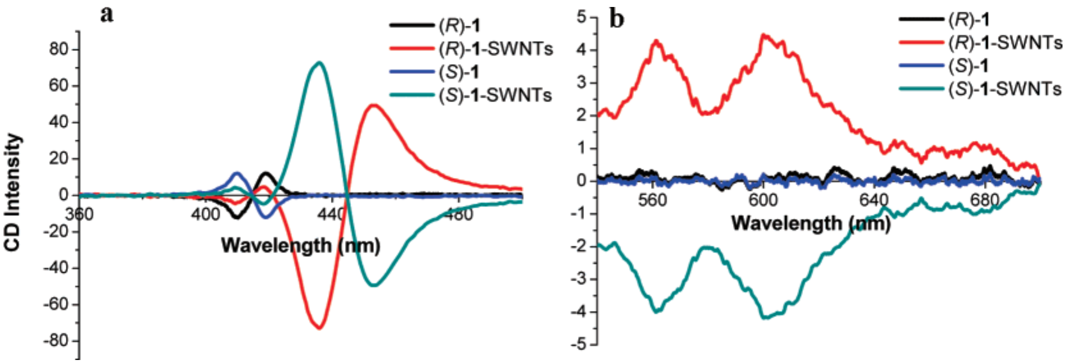

Figure 2. CD spectra of (*R*)-**1**, (*S*)-**1**, (*R*)-**1**:SWNTs and (*S*)-**1**:SWNTs in MeOH. All of the CD spectra were measured after their absorbance at 429 nm were normalized. The CD spectra in the range from 360 to 500 nm (a) and 540 to 700 nm (b) were measured using 1 and 10 cm cells, respectively.

Extraction of SWNTs with Chiral Nanotweezers. After SWNTs (CoMoCAT, SouthWest NanoTechnologies, Inc.)[10] in methanol were bath-sonicated in the presence of (*R*)- or (*S*)-**1**, the resulting suspension was centrifuged for 5 h to give black supernatant. As shown in Figure 1, the diporphyrins (*R*)-**1** and (*R*)-**2** exhibit split Soret bands at 412 and 429 nm, and 415 and 430 nm, respectively; but upon complexation with SWNTs, the Soret bands are considerably broadened, and the band peaks were red-shifted to around 450 nm. Similar spectral changes are observed in the Q-band region; the Q-bands of **1** at 550 nm and those of **2** at 553 nm are broadened and shifted to 600 nm upon complexation with SWNTs. These spectral changes in Figure 1 indicate strong $\pi-\pi$ interaction of the two porphyrin moieties of **1** and **2** with SWNTs. The much larger upward shift of the baseline in the absorption spectrum of (*R*)-**1**:SWNTs than that of (*R*)-**2**:SWNTs (Figure 1a) can be ascribed to the improved extraction ability of **1**, because the baseline shift is due mainly to Rayleigh scattering of the extracted SWNTs and, therefore, corresponds to the increased amount of SWNTs extracted. These results indicate a better SWNT extraction ability of **1**, which actually has been confirmed by the amount of extracted SWNTs. This will be described in detail below.

Optical Activity of Extracted SWNTs. The CD spectra of (*R*)-**1**, (*S*)-**1**, and their SWNT complexes are shown in Figure 2. (*R*)- and (*S*)-**1** display symmetrical bisignate Cotton effects at 410 and 419 nm (Figure 2a) which correspond to the Soret bands. This indicates that the two porphyrin subunits adopt an asymmetrical conformation induced by the four chiral substituents and that there is exciton coupling between them.[30−32] Upon complexation with SWNTs, a new set of symmetrical CD signals appear with strong intensity at longer wavelengths (436 and 452 nm), at the expense of the CD signals of the original (*R*)- and (*S*)-**1** free molecules. The positions of the new CD signals correspond to the Soret bands of the diporphyrins in the (*R*)- and (*S*)-**1**:SWNT complexes. The marked CD signal enhancement by the complexation can be attributed to the fixation of asymmetrical conformations of the two porphyrin moieties on the SWNT surface as depicted in the molecular models (Figure 6), which will be discussed below.[30−32] Both the red-shift of the CD and the increase of its intensity at the Soret band also support the above conclusion regarding the $\pi-\pi$ electronic interaction between porphyrin and SWNTs.

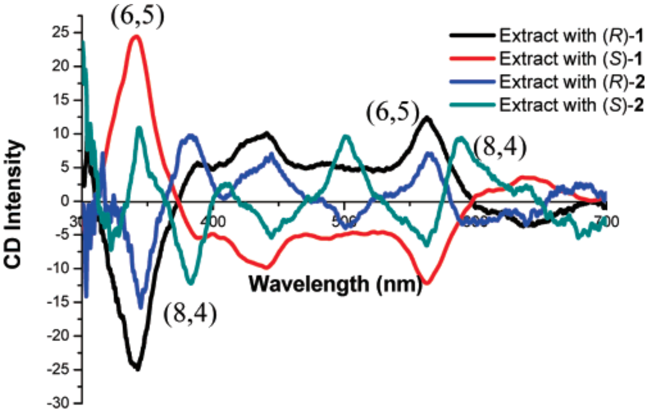

Figure 3. CD spectra of the D_2O/SDBS solutions of SWNTs extracted with (*R*)-**1**, (*S*)-**1**, (*R*)-**2**, and (*S*)-**2**. The SWNTs were recovered from the supernatant after centrifugation for 5 h and washed with pyridine several times to remove chiral diporphyrins completely. The concentrations of SWNTs in these solutions were normalized by their absorption peaks at 980 nm.

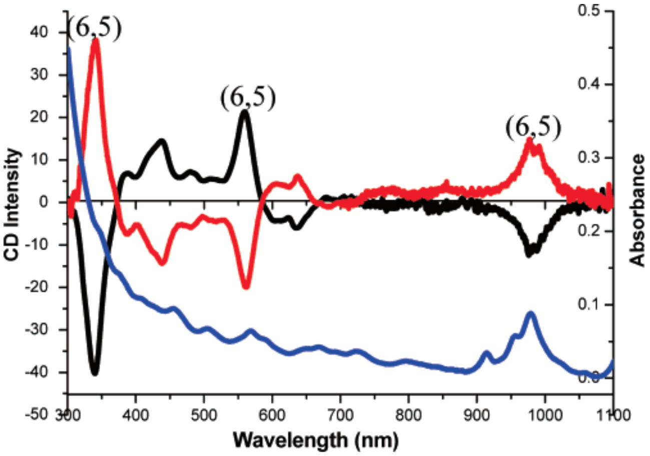

Figure 4. CD spectra of the D_2O/SDBS solutions of SWNTs extracted with (*R*)-**1** (black line) and (*S*)-**1** (red line), and UV−vis spectra of the D_2O/SDBS solution of SWNTs extracted with (*R*)-**1** (blue line). The SWNTs were recovered from the supernatant after centrifugation for 23 h and washed with pyridine several times to completely remove chiral diporphyrins. The concentrations of SWNTs in these solutions were normalized by their absorption peaks at 980 nm.

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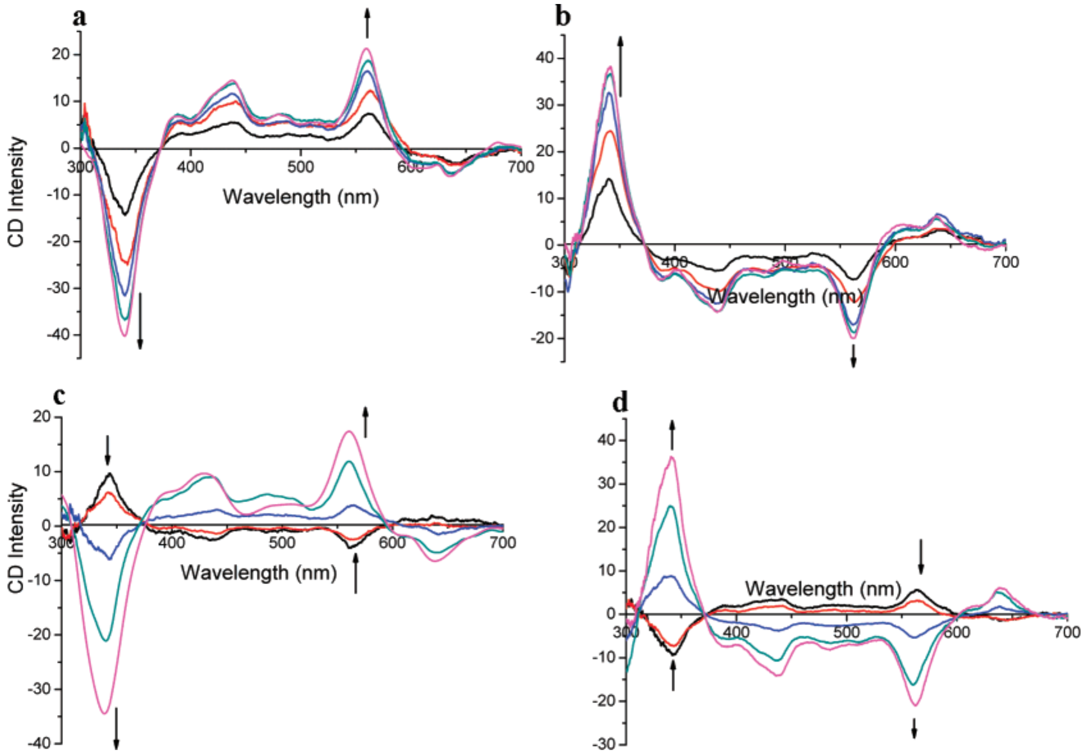

Figure 5. CD spectra of the D_2O/SDBS solutions of SWNTs extracted with (*R*)-**1** (a and c) and (*S*)-**1** (b and d) in the supernatants (a and b) and precipitates (c and d). The SWNTs were recovered from the supernatant and the precipitate after centrifugation for 2, 5, 9, 14, and 23 h, and washed with pyridine several times to completely remove chiral diporphyrins. The concentrations of SWNTs in these solutions were normalized by their absorption peaks at 980 nm. The arrows indicate the direction of the CD change according to centrifugation time.

(*R*)- and (*S*)-**1**:SWNT complexes also show clear and symmetrical CD signals at longer wavelengths (564 and 600 nm), as shown in Figure 2b. The intensity is much smaller than those corresponding to the Soret band. The CD signals of the complex at 564 and 600 nm are considered to originate from the E^S_{22} absorption band of (6,5)-SWNTs complexed with **1** and the Q-band of **1** complexed with SWNTs, respectively. This is because (6,5)-SWNTs are reported to have E^S_{22} absorption around 560 nm[33] and the **1**:SWNT complex is observed to have Q-band red-shifted to around 600 nm in Figure 1, as mentioned above. Free diporphyrin **1** does not exhibit any clear CD signal in this region, and thus, the appearance of the CD signal at 600 nm due to **1** upon complexation with SWNTs is considered to arise from fixation of its asymmetrical conformations.[30−32]

Taking advantage of the coordination between the porphyrinatozinc(II) and pyridine, we succeeded in removing the porphyrin nanotweezers completely from the complexes by washing with pyridine several times. After thorough removal of chiral nanotweezers from the complex,[24] the SWNTs were dissolved into D_2O with the aid of sodium *p*-dodecylbenzenesulfonate (SDBS)[34] and the resulting solutions were analyzed with CD. The solutions of SWNTs extracted by (*R*)- and (*S*)-diporphyrins show symmetrical CD spectra, as shown in Figure 3. Although the intensity of the peaks is not so different in SWNTs extracted with **2**, SWNTs extracted by **1** show two prominent CD peaks at 341 and 562 nm, corresponding to E_{33} and E_{22} transitions of the (6,5)-SWNTs, respectively.[33] These spectral features suggest a much higher discrimination ability of **1** to the helical structures of (6,5)-SWNTs, although the optical purity cannot be quantitatively determined. The CD signs corresponding to (6,5)-SWNTs are observed to be alternate at 341, 562, and 980 nm (Figure 4); that is, (+, −, +) for (6,5)-SWNTs extracted with (*S*)-**1** and (−, +, −) for those extracted with (*R*)-**1**. These alternate features are consistent with the theoretical prediction,[1,2,35,36] hence indicating optical activities of the extracted SWNTs.[24] The similar alternate spectral features are also observed for (8,4)-SWNTs at 386 and 603 nm that are assigned to E_{33} and E_{22} transitions (Figure 4).

The extraction abilities of **1** and **2** were quantified by measuring the amounts of porphyrin-free SWNTs in the extraction experiments. Tweezers **1** extracted ~50% of SWNTs, whereas tweezers **2** extracted less than 5% of SWNTs. This enhanced extraction ability of **1** can be attributed to the formation of more stable SWNT complexes in methanol.

The above results show that the change of the spacer in chiral nanotweezers greatly enhances the ability for extracting SWNTs and discriminating the helical structures of the SWNTs with specific roll-up indices. The choice of an appropriate spacer unit is found to be one of the most important factors for separating SWNTs.

Further Optical Enrichment. It is important to note that Figures 3 and 4 show the CD spectra of the extracted SWNTs only differing in centrifugation time, 5 and 23 h, respectively. We noted that longer centrifugation increased the optical activity of the SWNTs, as in the case of **2**.[24] Thus, we examined the effects of centrifugation time on the optical purity of SWNTs more carefully. We traced the CD intensity of both supernatants

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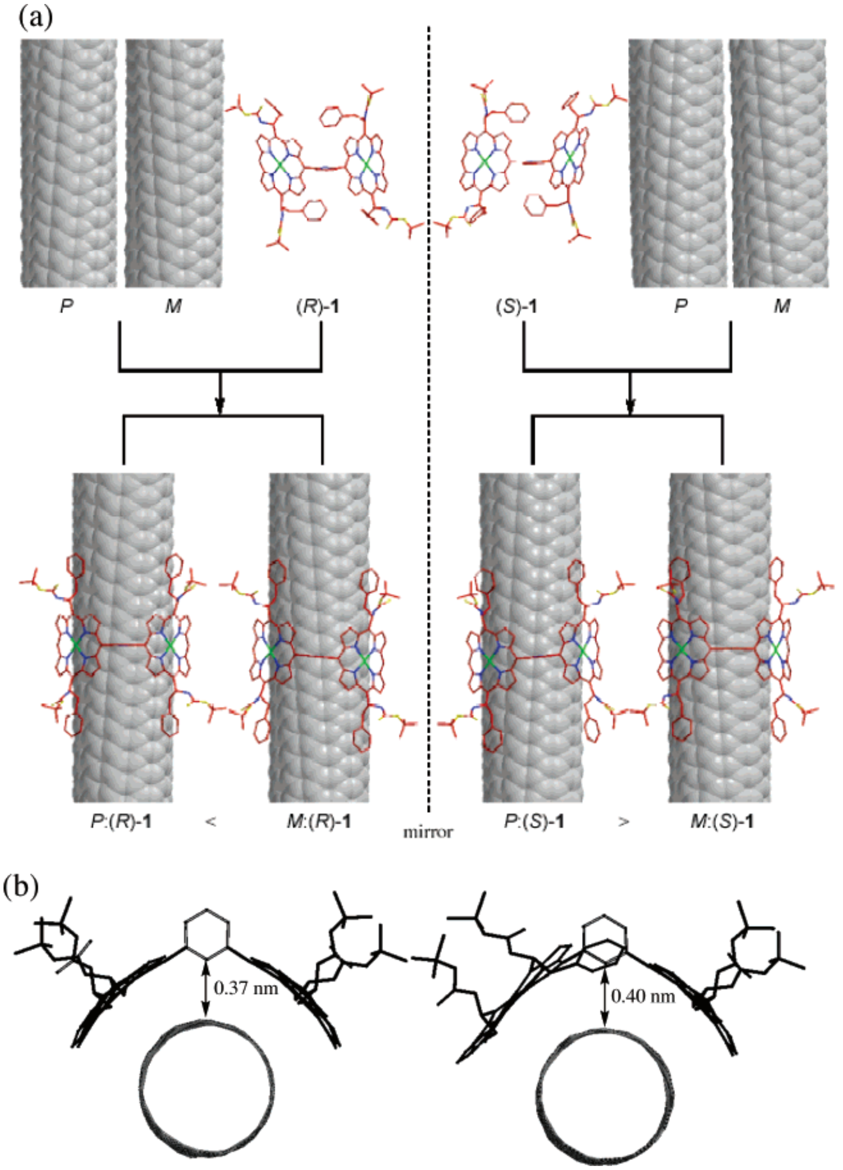

Figure 6. Computer-generated molecular modeling of the complex structures; (a) side views of 1:1 complexes of (*R*)- and (*S*)-**1** with (P)- and (*M*)-(6,5)-SWNTs, (b) views of 1:1 complexes of (*M*)-(6,5)-SWNTs with (*R*)-**1** (left) and (*R*)-**2** (right) along the SWNT axis.

and precipitates after centrifugation for 2, 5, 9, 14, and 23 h. The supernatants were concentrated, washed with pyridine several times, and dissolved in SDBS/D_2O to prepare a sample solution for the CD measurement, and the precipitates were washed with pyridine several times, and dissolved in SDBS/D_2O to prepare a sample solution. For the CD measurements, the concentration of (6,5)-SWNTs in these solutions was normalized at the absorbance of 980 nm (Figure 5).

Remarkably, prolonged centrifugation causes progressive enrichment of optical purities of SWNTs in the supernatants, as indicated by the arrows in Figure 5, parts a and b. The CD intensity of the last supernatant (23 h centrifugation) is about 3 times larger than that of the first supernatant (2 h centrifugation), meaning that the optical purity of the SWNTs in the supernatant improves significantly by centrifugation from that just after extraction. However, the improvement in optical purity becomes smaller and smaller as centrifugation proceeds. The precipitates obtained after centrifugation for 2 and 5 h show the opposite CD signals of the supernatants, but those obtained for 9, 14, and 23 h show the same CD signals. Finally, the supernatants and precipitates obtained after centrifugation for 23 h exhibit nearly the same CD intensity, suggesting that the optical purity of SWNTs is almost saturated.

This enrichment can be accounted for in terms of the dynamic nature of noncovalent interactions of **1** with SWNTs. The more stable complex of **1**, with one optical isomer, is enriched through the dynamic sorting of the complex with the other one. In other words, less stable complexes tend to dissociate in solution, which precipitate out more efficiently during centrifugation.

Theoretical Calculations for Complex Structures. For the theoretical support and interpretation of the above experimental results, we carried out molecular modeling calculations (molecular mechanics) for the complexes of (*P*)- and (*M*)-(6,5)-SWNTs (simply designated as *P* and *M*, respectively) with (*R*)- and (*S*)-**1**. The structures are shown in Figure 6, parts a and b.

In Figure 6a, two sets of enantiomers, *P*:(*R*)- and *M*:(*S*)-**1**, and *P*:(*S*)- and *M*:(*R*)-**1**, show highly symmetrical mirror-images, and two sets of diastereomers, *P*: and *M*:(*S*)-**1** and *P*: and

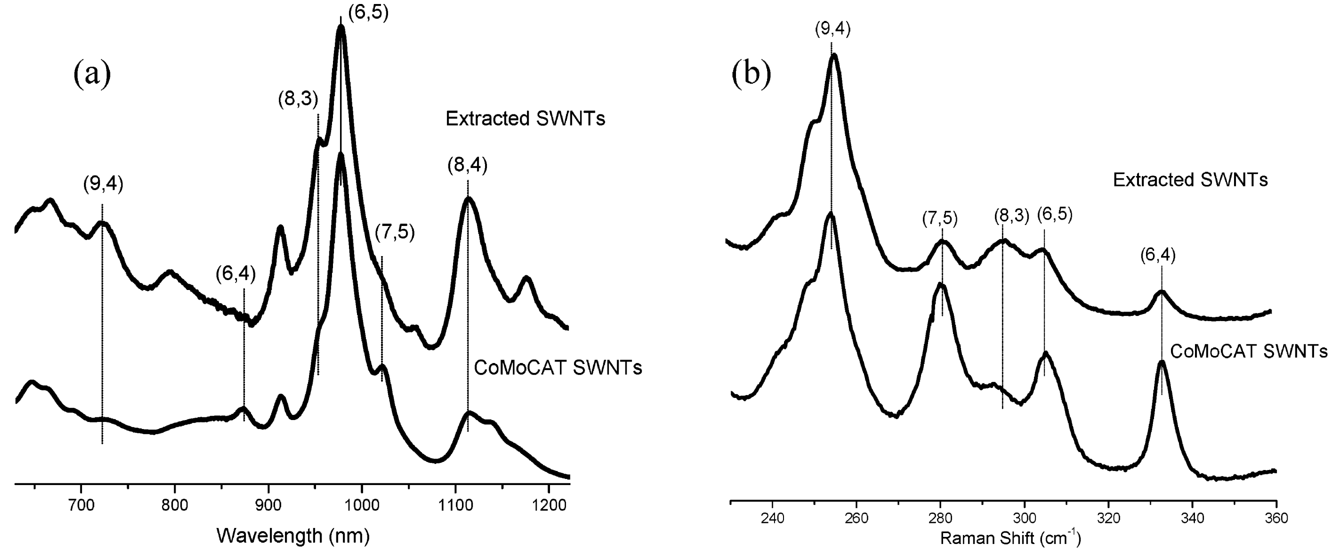

Figure 7. Qualitative evaluation of semiconducting (*n*, *m*) abundance before and after extraction with (*R*)-**1** by (a) Vis-NIR spectra of D_2O/SDBS solutions of CoMoCAT SWNTs and extracted SWNTs and (b) Raman spectra of their solid samples at the excitation of 633 nm. In both spectra, SWNTs extracted with (*S*)-**1** gave almost the same spectra. The bands shown in the spectra are assigned by calculated values reported in refs 37 and 38.

M:(*R*)-**1**, show different structures. Two porphyrin planes in each complex adopt an asymmetrical conformation, which is consistent with the observed bisignate Cotton effect at the Soret bands (Figure 2a). The association enthalpies in *P*:(*R*)-**1**, *M*:(*R*)-**1**, *P*:(*S*)-**1**, and *M*:(*S*)-**1** are calculated to be −57.78, −58.00, −58.00, and −57.78 kcal mol^{-1}, respectively. The identical magnitudes of the energy between the enantiomers reinforce the validity of this calculation. The difference in the energy between the diastereomers suggests that *M* and *P* are enriched by use of (*R*)-**1** and (*S*)-**1**, respectively. The same preference to the handedness of (6,5)-SWNTs was observed in the case of **2**, as reported in our previous paper.[24]

In the complex structures depicted in Figure 6b, the 2,6-pyridylene-bridged nanotweezers **1** fit very nicely along the curvature of the SWNT at a distance of 0.37 nm, with the two porphyrin moieties bent. In addition, the four phenyl groups in the side chains are favorably interacting with the surface of the SWNT at an interplanar distance of 0.37 nm. All of these interactions should be $\pi-\pi$ interactions because of the distances between the two π-planes facing each other. In the complex of **2**, however, the shape compatibility of the porphyrin plane with the SWNT curvature is a little less than that of **1**, and only three phenyl groups out of four come close to the SWNT surface, making the *M*:(*R*)-**2** less stable than the *M*:(*R*)-**1**. This structural difference between complexes is quantitatively explained by the theoretical calculations; the association enthalpies for *M*:(*R*)-**1** and *M*:(*R*)-**2** are −58.00 and −56.36 kcal mol^{-1}, respectively.

The distance between the spacer unit of the nanotweezers and the surface of SWNT is also different between these complexes. As shown in Figure 6b, the distance between the nitrogen atom in the pyridylene spacer and SWNT surface is 0.37 nm in *M*:(*R*)-**1**, whereas the distance between the carbon atom at the 2-position of the benzene ring and SWNT surface is 0.40 nm in *M*:(*R*)-**2**. (6,5)-SWNT enters the cavity of **1** deeply to stabilize the complex, whereas the cavity of **2** cannot accommodate the SWNT as well as that of **1** because of the steric hindrance of the hydrogen atom at the 2-position of the benzene ring and the larger dihedral angle of the two porphyrin planes in **2** (111.2°) compared to that in **1** (93.8°). This also results in the destabilization of the complex of **2** as compared to that of **1**.

The change in the porphyrin dihedral angles by complexation also increases the difference in stability; the dihedral angles of the two porphyrin planes, 93.8° in **1** and 111.2° in **2**, change to 94.6° and 94.1°, respectively. The angle in **1** remains almost the same before and after complexation. However, **2** makes the angle smaller to interact with the SWNT surface, providing considerable stress to the complex of **2** to reduce the stability.

The above-discussed stability difference in the complex structures should cause the difference in the extraction and discrimination ability between the 2,6-pyridylene- and 1,3-phenylene-bridged nanotweezers.

Qualitative Comparison in (*n*, *m*) Abundance of Semiconducting SWNTs before and after Extraction. Although optical enrichment of SWNTs, namely *M* and *P* abundance, has been discussed so far, the (*n*, *m*) abundance of SWNTs should also be changed through the extraction. The relative population among several semiconducting SWNTs is compared qualitatively in Vis-NIR and Raman spectra (Figure 7, parts a and b, respectively) before and after the extraction with (*R*)-**1**. The solution of CoMoCAT SWNTs for the absorption spectrum was prepared by use of D_2O and SDBS in the same procedure as that of the extracted SWNTs mentioned above.[34] The following solid samples were subjected to resonant Raman spectroscopy: as-received CoMoCAT SWNTs and extracted SWNTs after removal of nanotweezers by washing with pyridine. In both Vis-NIR and Raman spectra, SWNTs extracted with (*S*)-**1** gave almost the same spectra as those obtained from SWNTs extracted with (*R*)-**1**.

The changes in the relative (*n*, *m*) abundance of semiconducting SWNTs before and after extraction are evaluated qualitatively in Vis-NIR and Raman spectra, and the results are summarized in Table 1. The six typical semiconducting CoMoCAT SWNTs, (6,4), (6,5), (7,5), (8,3), (8,4), and (9,4), are assigned by the absorbance in the region of λ_{11} or λ_{22} (the first or second optical transition energy) in the Vis-NIR spectra (Figure 7a),[37] and the bands in the region of radial breathing mode in Raman

Table 1. Relative Change in (*n*, *m*) Abundance of Semiconducting SWNTs after Extraction with (*R*)-**1**

roll-up index	roll-up angle (deg)	diameter (nm)	Vis-NIR λ_{11} (nm)[a]	Vis-NIR relative abundance[b]	Raman ω (cm^{-1})[c]	Raman relative abundance[b]
(8,3)	15.3	0.78	955 (952)	+	297 (298)	+
(9,4)	17.5	0.92	723[d] (722)	+	256 (257)	+
(8,4)	19.1	0.84	1116 (1111)	+	−[e] (279)	
(6,4)	23.4	0.76	874 (873)	−	334 (335)	−
(7,5)	24.5	0.83	1023 (1024)	−	282 (282)	−
(6,5)	27.0	0.76	981 (976)	−	306 (308)	−

[a] Values in parentheses indicate predicted ones reported in ref 37. [b] Signs of “+” and “−” indicate that the abundance of the given (*n*, *m*) SWNT relatively increased and decreased, respectively, after extraction. [c] Values in parentheses indicate predicted ones reported in ref 38. [d] λ_{22}. [e] The Raman band corresponding to (8, 4) was not able to find in Figure 7b.

spectra (Figure 7b).[38] As a result, (8,3), (8,4), and (9,4) SWNTs having smaller roll-up angles were relatively enriched, and, in contrast, the relative abundance of (6,4), (6,5), and (7,5) SWNTs having larger roll-up angles decreased through the extraction. This result shows that the nanotweezers (**1**) discriminate by the alignment of the hexagons rather than by the difference in the degree of the curvature of these SWNTs.

Taking the above-discussed optical enrichment into account, we can conclude that while the abundance of (6,5)-SWNTs decreased relatively among the six semiconducting SWNTs through the extraction with **1**, they were optically enriched more pronouncedly than the other SWNTs. The relatively high optical purity of (6,5)-SWNTs indicates that **1** can recognize the alignment of the hexagons in terms of not only pitch, but also handedness. The decrease in the relative abundance of (6,5)-SWNTs can be attributed to their relatively high optical purity. For example, precipitation of a large amount of one optical isomer in one (*n*, *m*) SWNTs results in high optical purity, but significantly reduces the total amount of the (*n*, *m*) SWNTs. Alternatively, precipitation of the other (*n*, *m*) SWNTs in a small amount gives low optical purity, but increases the relative abundance.

Conclusion

Optically enriched SWNTs were successfully obtained through preferential extraction of one of the helical structures in each roll-up index of chiral SWNTs with newly designed chiral nanotweezers. The nanotweezers **1**, consisting of two chiral porphyrin moieties bridged by a 2,6-pydiylene spacer show much improved SWNTs extraction ability than the 1,3-phenylene-bridged ones **2**. In addition, the CD intensity of the specific SWNTs extracted with **1** is much higher than those extracted with **2**. These features of the newly designed nanotweezers are ascribed to the stable complex formation, which is supported by the comparison of the computer-generated complex structures.

Our goal is to obtain carbon nanotubes with single structure, namely, single roll-up index with single helicity, in bulk quantity. The present finding of the enhancement in the ability of the nanotweezers by changing the spacer gives us an important guide to achieve this goal.

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Supporting Information Available: Experimental details, including synthesis of (*R*)- and (*S*)-**1** and extraction procedures, and complete ref 22. This material is available free of charge via the Internet at http://pubs.acs.org.

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