Simultaneous Enrichments of Optical Purity and (*n,m*) Abundance of SWNTs through Extraction with 3,6-Carbazolylene-Bridged Chiral Diporphyrin Nanotweezers

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Single-walled carbon nanotubes (SWNTs) are currently the focus of great interest because of their unique physical and chemical properties.[1] For their further development in fundamental science and technological applications, structural control of SWNTs is very important, as the electronic and optical properties are largely determined by their structures.[2] Therefore, selective synthesis and separation of SWNTs have been extensively investigated,[3] and the past few years have seen remarkable progress in obtaining specific structures of SWNTs selectively. SWNTs with narrow distribution in (*n,m*) have been grown by chemical vapor deposition (CVD) on a Ru−Fe catalyst at various temperatures,[4] a Co−Mo catalyst with various carbon sources,[5] and a silica-templated Co catalyst (Co-MCM-41).[6] Sorting methods of SWNTs have been also developed by ultracentrifugation of surfactant-encapsulated SWNTs,[7−10] ion exchange chromatography of DNA-wrapped SWNTs,[4,6,11,12] and selective extraction of SWNTs with aromatic polymers.[13−15] However, the chiral SWNTs thus synthesized or sorted still contain a pair of left- and right-handed helical forms (*M* and *P*, respectively, defined in our previous papers[16−19]) in equal amounts.[20] There have been no reports on optically active SWNTs, namely, SWNTs enriched in either *M* or *P* structure. Optically active SWNTs are expected to have inherent unique properties leading to technological applications in photonics, quantum optics, and photoelectronics; for example, photogalvanic effects with circularly polarized light were predicted theoretically.[21,22]

We have been developing a separation approach based on molecular recognition using chiral gable-type diporphyrins designated as "nanotweezers". This method allowed us to obtain optically active SWNTs for the first time.[16,23] Distinct advantages of our approach lie in the flexibility in molecular design of the nanotweezers for discrimination of not only left- and right-handed structures but also (*n,m*) structures of SWNTs and easy liberation of the nanotweezers from the complex by simple washing to recover the pristine SWNTs. We also found that a subtle change in the structure of nanotweezers strongly affects the discrimination ability; that is, much improved

ABSTRACT Since structural control of single-walled carbon nanotubes (SWNTs) leads to control of their physical properties, isolation and synthesis of specific (*n,m*) structures of SWNTs have been extensively investigated in view of their technological applications. In this context, we developed a novel method for separating SWNTs through molecular recognition with chiral gable-type diporphyrins designated as "nanotweezers". The method allowed us to obtain optically active SWNTs, namely, the chiral SWNTs enriched in either left- or right-handed helical form, for the first time. In this paper, we describe prominent optical enrichment of (7,5)-SWNTs through preferential extraction with chiral 3,6-carbazolylene-bridged nanotweezers as well as simultaneous enrichment of the abundance of (7,5)- and (8,4)-SWNTs. The (*n,m*) enrichment through this extraction is considered to result from the diameter differentiation of the nanotweezers, suggested by the complex structures in the theoretical calculations. That is, carbazolylene-bridged nanotweezers encapsulate a SWNT deeply enough to recognize the diameter of (7,5)-SWNTs. The deep contact is considered to realize the discrimination of the small diameter difference even less than 0.10 nm. This is a significant progress toward the separation of single species of SWNTs consisting of single (*n,m*) structure with one helicity.
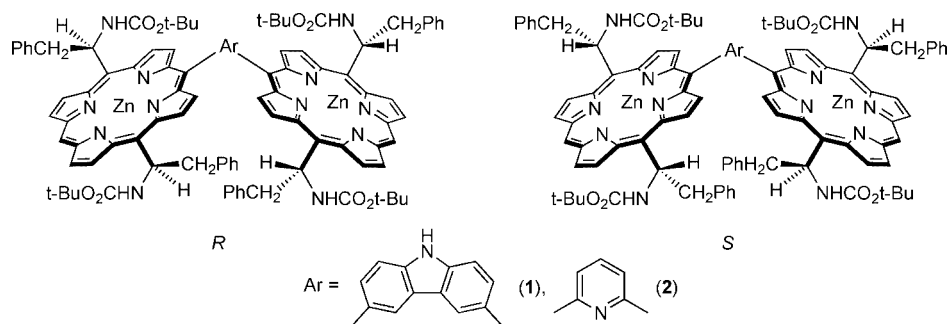
Chart 1. A pair of stereoisomers (*R* and *S*) of chiral diporphyrin nanotweezers 1 and 2.

optical enrichment was observed in (6,5)-SWNTs by changing the spacer in the nanotweezers from *m*-phenylene to 2,6-pyridylene.[16] In this paper, we describe prominent optical enrichment of (7,5)-SWNTs through preferential extraction with chiral 3,6-carbazolylene-bridged nanotweezers 1 (Chart 1) as well as simultaneous enrichment of the abundance of (7,5)- and (8,4)-SWNTs. This is a significant progress toward the separation of single species of SWNTs consisting of single (*n,m*) structure with one helicity.

RESULTS AND DISCUSSION

Chiral diporphyrin nanotweezers (*R*)- and (*S*)-1 were synthesized *via* Suzuki—Miyaura coupling reaction of the corresponding boronated (*R*)- and (*S*)-monoporphyrin with 3,6-dibromo-9*H*-carbazole (Supporting Information).[16,23] After bath sonication of a suspension of SWNTs in the presence of 1 followed by centrifugation, SWNTs were extracted in the supernatant through complexation with 1, which was confirmed by the absorption and the circular dichroism (CD) spectra (Supporting Information Figure S2).[16,23] After thorough removal of the chiral nanotweezers from the complex by washing with pyridine, the SWNTs were dissolved in D$_2$O/SDBS and subjected to CD measurement as well as absorption and resonant Raman spectroscopies to see the preference of 1 for the helicity and (*n,m*) abundance in SWNTs. The extraction procedure will be described in detail in Methods. Since an amount of the extracted SWNTs is less than 0.5 mg, we were not able to carry out further extraction for the SWNT extract to improve the optical purity and (*n,m*) abundance.

In the CD spectra shown in Figure 1, SWNTs extracted with (*R*)- and (*S*)-1 provide symmetric and opposite CD signals, indicating that two stereoisomers of 1, *R* and *S*, preferentially extracted SWNTs with different helicities, *M* and *P*,[16−19] and that the extracted SWNTs are optically active. The two dominant CD peaks at 639 and 374 nm are assigned to E$^S_{22}$ and E$^S_{33}$ transitions of the (7,5)-SWNTs, respectively.[23,24] This indicates that the helicity in (7,5)-SWNTs was discriminated by 1 to give optically enriched (7,5)-SWNTs, while other (*n,m*)-SWNTs were not optically enriched so much. Upon the extraction with 2, on the other hand, (6,5)-SWNTs were optically enriched much more than other (*n,m*)-

SWNTs.[16] Although the structures of (7,5) and (6,5) are not so different in terms of diameters (0.07 nm difference) and roll-up angles (2.5° difference), as shown in Table 1, the most optically enriched SWNTs were changed from (6,5) to (7,5) by just changing the spacer from pyridylene to carbazolylene. This indicates that nanotweezers can differentiate subtle structural difference between SWNTs. This result also supports the previous finding that change in the structure of the nanotweezers influences the structure of SWNTs extracted preferentially.[16]

The (*n,m*) abundance of SWNTs is compared in absorption and Raman spectra of as-received SWNTs (Co-MoCAT, SouthWest NanoTechnologies, Inc.)[25] and SWNTs extracted with (*R*)-1 as shown in Figure 2 and Table 2. The six typical semiconducting SWNTs, (6,4), (6,5), (7,5), (8,3), (8,4), and (9,4), are assigned by the bands in the region of E$^S_{11}$ in the absorption spectra (Figure 2a) and/or the bands in the region of radial breathing mode (RBM) in Raman spectra (Figure 2b).[24,26] The abundance of these SWNTs in Table 2 is determined by deconvolution of the vis—NIR and Raman spectra (Figure 2a,b) shown in Figures S3 and S4 in the Supporting Information, respectively. In the absorption spectra, the abundance of (7,5)- and (8,4)-SWNTs is relatively increased, while that of (6,5) is largely decreased. The Raman spectra indicate relative increase in the abundance of (7,5)-SWNTs and relative decrease of (6,4)-, (6,5)-, and (9,4)-SWNTs through the extraction with 1. The abundance of (8,3)-SWNTs is not so different before and after the extraction. From these spectra, it is concluded that the abundance of (7,5)- and (8,4)-SWNTs is increased and that of (6,4)-, (6,5)-, and (9,4)-SWNTs is decreased after the extraction. Although the selectivity for (*n,m*) is not so good as that in similar methods of selective extraction using fluorene-based
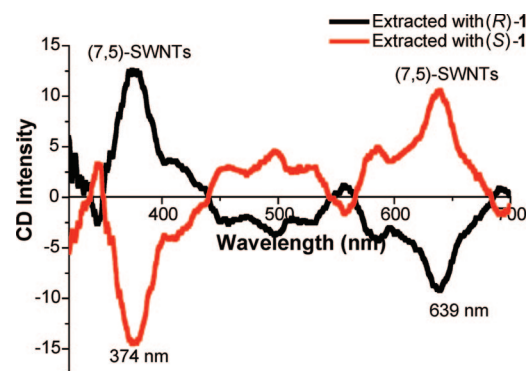

Figure 1. CD spectra of the D$_2$O/SDBS solutions of SWNTs extracted with (*R*)-1 (black line) and (*S*)-1 (red line). The concentration of SWNTs in the solutions was normalized by their absorption peaks at 1024.5 nm.

polymers[13,14] and flavin mononucleotide,[15] our chiral nanotweezers are bifunctional in that they discriminate not only the (n,m) but also the helicity of SWNTs.

These results of the optical and (n,m) enrichments mentioned above are summarized in Figure 3a. This figure clearly shows that the diameter of the SWNTs was distinguished, resulting in the (n,m) enrichment. That is, (7,5)- and (8,4)-SWNTs having similar diameters of 0.83 and 0.84 nm, respectively, are enriched, while SWNTs with smaller and larger diameters such as (6,4), (6,5), and (9,4) are not favored. On the other hand, the preference of **1** for the SWNTs having similar roll-up angles such as (6,4) and (7,5) is distinctly different; (7,5)-SWNTs are increased, while (6,4)-SWNTs are decreased through the extraction. This is in marked contrast with the case of the (n,m) selection with **2**, where (8,3)-, (8,4)-, and (9,4)-SWNTs with smaller roll-up angles (15.3−19.1°) are preferentially extracted, but (6,4), (6,5), and (7,5) with larger roll-up angles (23.4−27.0°) are not favored as illustrated in Figure 3b.[16] Since the diameter differences between (7,5) and (6,5), and (8,4) and (9,4) are calculated to be 0.07 and 0.08 nm, respectively (Table 1), the experimental results of the enrichment of (7,5)- and (8,4)-SWNTs indicate that the nanotweezers **1** can distinguish less than 0.10 nm difference in the diameters of SWNTs. The precise differentiation of the diameters can be ascribed to the complex structure, which will be discussed in detail below.

The enrichment in both (n,m) abundance and optical purity of (7,5)-SWNTs upon extraction with **1** is also supported by computer-generated molecular models of the complexes of (R)-**1** with (6,5)-, (7,5)-, (8,3)-, (8,4)-, and (9,4)-SWNTs. The nanotweezers **1** have a smaller dihedral angle (74.2°) and a longer bridge length (0.61 nm between 3,6-positions in the carbazolylene bridge) as compared with **2** which has a dihedral angle of 93.8° and a bridge length of 0.23 nm. Such structural character of **1** enables much deeper accommodation of

TABLE 1. Roll-Up Angles and Diameters of Typical SWNTs and Center-to-Center Distances between Two Zinc Atoms of (R)-1 before and after Complexation with (M)-(n,m)-SWNTs[a]

	(R)-1	(6,4)	(6,5)	(8,3)	(7,5)	(8,4)	(9,4)
roll-up angle (deg)		23.4	27.0	15.3	24.5	19.1	17.5
diameter (nm)		0.69	0.76	0.78	0.83	0.84	0.92
distance (nm)[b]	1.27[c]	1.22[d]	1.24[d]	1.25[d]	1.27[d]	1.27[d]	1.29[d]

[a]Molecular mechanics calculation. [b]The distances are the same as those of their enantiomers, (S)-**1** and (S)-**1**:(P)-(n,m)-SWNT complexes. [c]The distance before complexation. [d]The distance after complexation with the given SWNT.

SWNTs as shown in Figure 4a, making precise differentiation of diameter possible. On the other hand, a shallower contact is only possible for **2** as shown in Figure 4b, making the recognition of diameter very difficult.

Further, almost no additional structural changes of **1** are needed upon complexation with (7,5)- and (8,4)-SWNTs (0.83 and 0.84 nm in diameter, respectively), while some structural adjustments of **1** are required for accommodation of other SWNTs with larger and smaller diameters as shown in Table 1. The center-to-center distance between the two zinc metals in the diporphyrin nanotweezers (R)-**1** (1.27 nm) hardly changes after the complexation with (M)-(7,5)- and (M)-(8,4)-SWNTs. On the other hand, the center-to-center distances have to be either smaller (1.22−1.25 nm) upon the complexation with (M)-(6,4)-, (M)-(6,5)-, and (M)-(8,3)-SWNTs or larger (1.29 nm) upon the complexation with (M)-(9,4)-SWNTs. Such deformations would destabilize these complexes and, therefore, enable **1** to distinguish the diameters of SWNTs. These results of the theoretical calculations are consistent with those of the experiments mentioned above, indicating that we can predict the diameter of SWNTs that will be preferentially extracted by the designed nanotweezers. In other words, nanotweezers can be tailored to the specific diameter of SWNTs based on computer simulations.
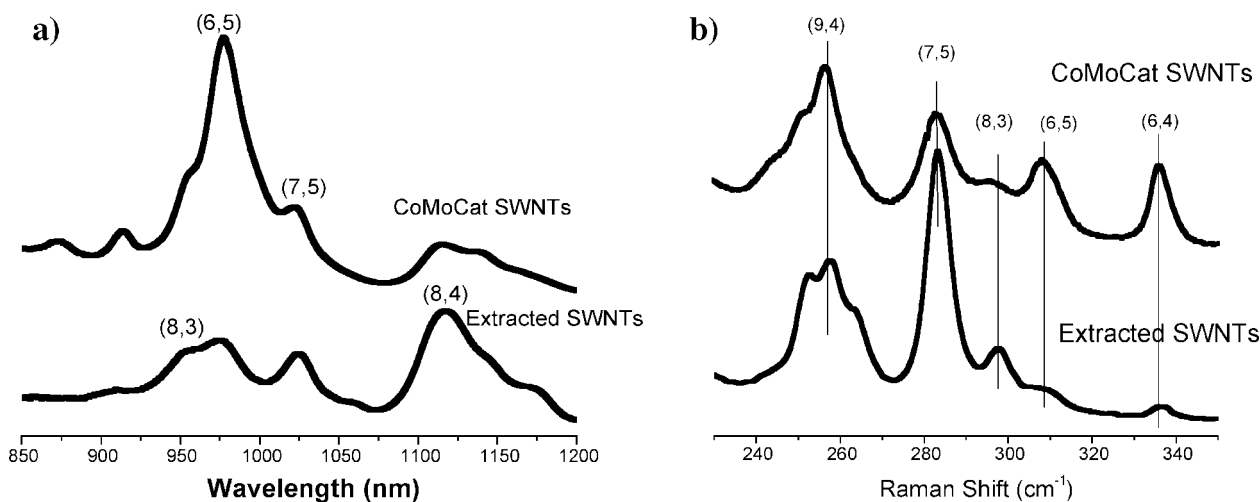

Figure 2. (a) Vis−NIR spectra of D₂O/SDBS solutions of CoMoCAT SWNTs and extracted SWNTs, and (b) Raman spectra of their solid samples at the excitation of 633 nm. In both spectra, SWNTs extracted with (S)-**1** gave almost the same spectra. The bands shown in the spectra are assigned by calculated values reported in refs 24 and 26.

TABLE 2. (n,m) Abundance of Semiconducting SWNTs before and after Extraction with (R)-1[a]

roll-up index	vis−NIR			Raman		
	λ_{11} (nm)[b]	abundance (%) in CoMoCAT	abundance (%) in extract	ω (cm^{-1})[c]	abundance (%) in CoMoCAT	abundance (%) in extract
(6,4)				336 (335)	28	2
(6,5)	978 (976)	56	23	308 (308)	16	4
(8,3)	954 (952)	19	16	296 (298)	10	13
(7,5)	1024 (1024)	17	21	283 (282)	25	58
(8,4)	1116 (1111)	28	40			
(9,4)				257 (257)	31	23

[a]The (n,m) abundance was determined by deconvolution of vis−NIR and Raman spectra (Figures S3 and S4 in the Supporting Information). [b]Values in parentheses indicate predicted ones reported in ref 24. [c]Values in parentheses indicate predicted ones reported in ref 26.

As for the optical enrichment, complex structures of (R)-**1**:(M)-(7,5), (R)-**1**:(P)-(7,5), (S)-**1**:(M)-(7,5), and (S)-**1**:(P)-(7,5) were calculated with molecular mechanics (Figure 5a). Each pair of the enantiomers, (R)-**1**:(M)-(7,5) and (S)-**1**:(P)-(7,5), and (R)-**1**:(P)-(7,5) and (S)-**1**:(M)-(7,5), exhibited the same magnitudes of enthalpy change, −62.64 and −62.33 kcal/mol, respectively. The difference in the enthalpy change of the diastereomers (0.31 kcal/mol) resulted in the optical enrichment of the more stable complex, (R)-**1**:(M)-(7,5) or (S)-**1**:(P)-(7,5), in the supernatant and the less stable complex, (R)-**1**:(P)-(7,5) or (S)-**1**:(M)-(7,5), 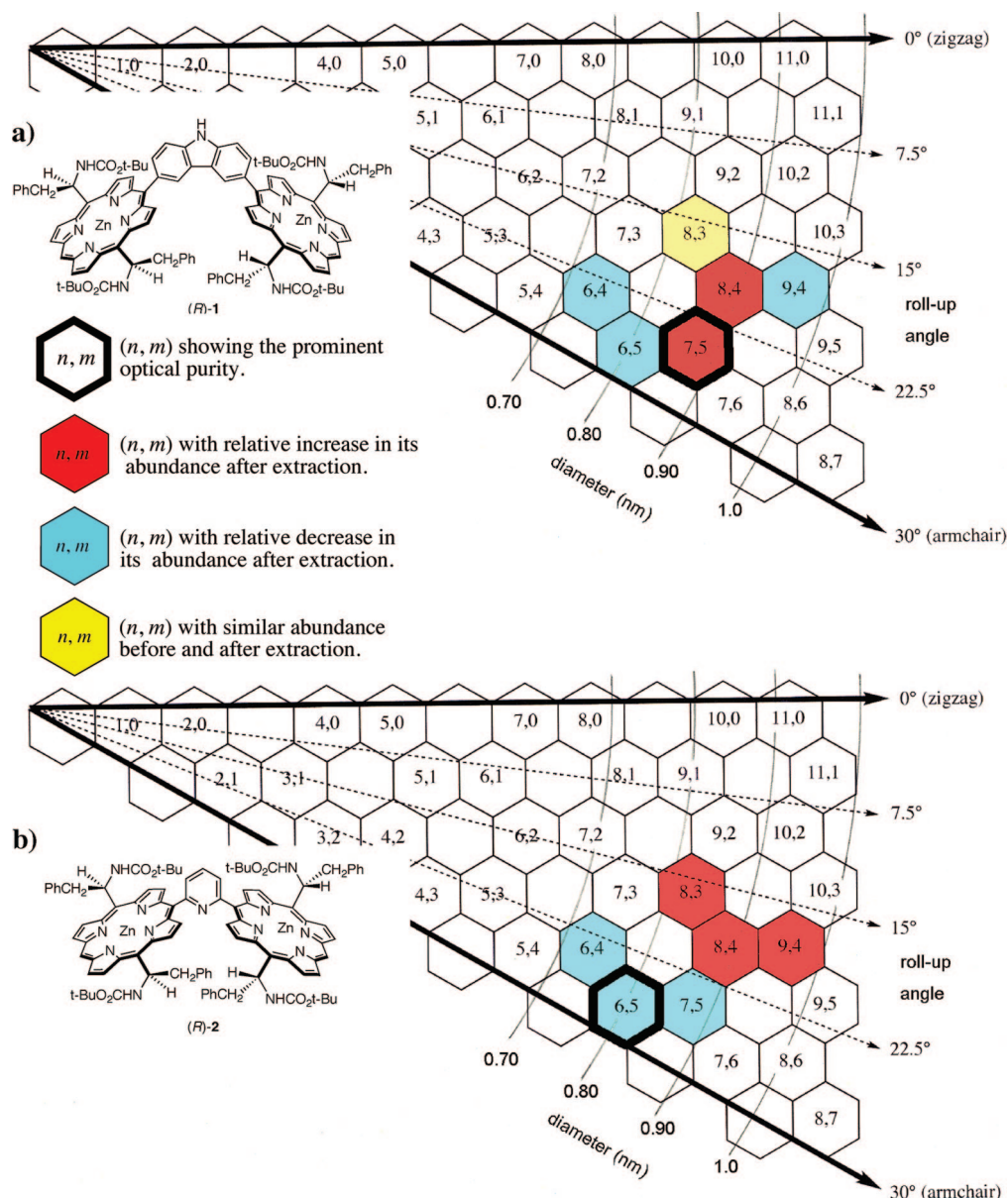in the precipitates. The results indicate that (R)- and (S)-**1** preferentially extract (M)- and (P)-(7,5)-SWNTs, respectively, which is the same preference of the previously reported nanotweezers to the helicity of (6,5)-SWNTs.[16,23]

Figure 3. Summary of enrichment in (n,m) abundance and optical purity in the extraction of SWNTs with (R)-**1** (a) and (R)-**2** (b).
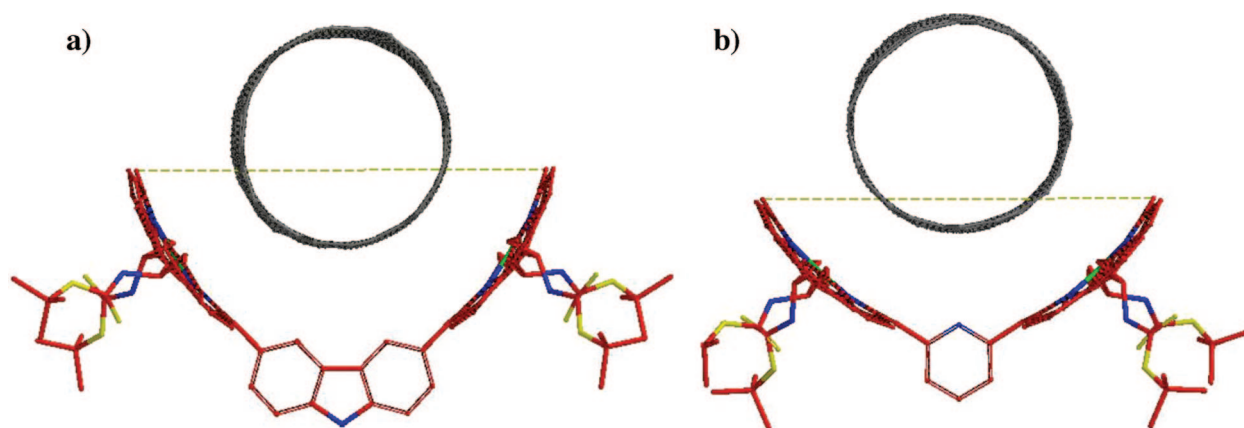
Figure 4. Computer-generated molecular models of the complexes of (*R*)-1 (a) and (*R*)-2 (b) with (*M*)-(7,5)-SWNTs.

The nanotweezers **1** were calculated to behave in a similar manner toward (8,4)-SWNTs; the enantiomers, (*R*)-**1**:(*M*)-(8,4) and (*S*)-**1**:(*P*)-(8,4), showing −63.33 kcal/mol enthalpy change are more stable than the ones, (*R*)-**1**:(*P*)-(8,4) and (*S*)-**1**:(*M*)-(8,4), showing −63.07 kcal/mol enthalpy change. The difference in the enthalpy change of the diastereomers (0.26 kcal/mol) is smaller than that of (7,5)-SWNTs (0.31 kcal/mol), leading to the lower optical activity of (8,4) than that of (7,5). In addition, the conformations of **1** are not so different between the diastereomers, (*R*)-**1**:(*M*)-(8,4) and (*R*)-**1**:(*P*)-(8,4), and (*S*)-**1**:(*M*)-(8,4) and (*S*)-**1**:(*P*)-(8,4), as shown in Figure 5b. This is in marked contrast with the case of (7,5), where **1** adopts different conformations upon complexation with (*M*)- and (*P*)-SWNTs as shown in Figure 5a. This implies that the nanotweezers **1** cannot recognize the helicities of (8,4)-SWNTs so well, supporting the experimental result of lower CD intensities of (8,4) than those of (7,5) shown in Figure 1.

Figure 5. Computer-generated complex structures of (*R*)- and (*S*)-1 with (*M*)- and (*P*)-(7,5)-SWNTs (a) and with (*M*)- and (*P*)-(8,4)-SWNTs (b).

changed from (6,5)- to (7,5)-SWNTs, in spite of their subtle structural difference, by changing the spacer in the nanotweezers from 2,6-pyridylene to 3,6-carbazolylene. The (*n,m*) enrichment in this extraction is considered to result from the diameter differentiation of the nanotweezers, which is suggested by the complex structure in theoretical calculations. The 3,6-carbazolylene-bridged nanotweezers **1** embrace (7,5)-SWNT deeply enough to recognize the size of the SWNT. The deep contact is considered to realize the discrimination of their small diameter difference (less than 0.10 nm). This is a significant step toward the ultimate separation of single species of SWNTs in terms of diameter and helicity.

CONCLUSIONS

(7,5)-SWNTs are simultaneously enriched in their optical purity and abundance through the extraction with the 3,6-carbazolylene-bridged chiral diporphyrin nanotweezers **1**, though the abundance of (8,4)-SWNTs is also increased. The most optically enriched SWNTs are
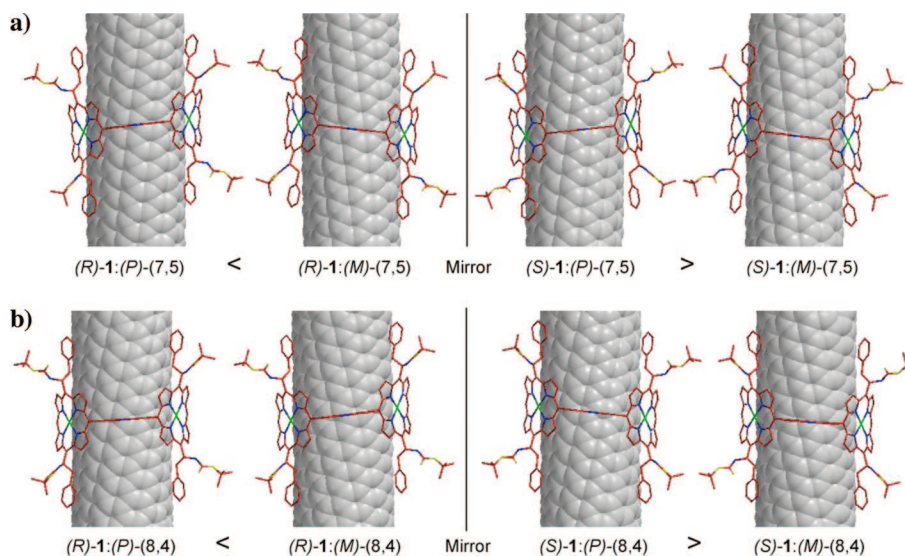
METHODS

Extraction of SWNTs with 1. SWNTs (10 mg, CoMoCAT, SouthWest NanoTechnologies, Inc.) and (*R*)- or (*S*)-**1** (5 mg) in methanol (20 mL) were bath-sonicated at 20 °C for 5 h. After the resulting suspension was centrifuged at 50 400*g* for 5 h, the

supernatant was subjected to UV−vis−NIR and CD measurements (Figure S2 in the Supporting Information). After concentration of the supernatant, the residue was washed with pyridine several times until the porphyrin Soret band disappeared in the UV−vis spectra of the washings. The thoroughly washed SWNTs

were analyzed with Raman spectroscopy (Figure 2b) and dispersed into D_2O (18.5 mL) in the presence of SDBS (10 mg/mL) by tip-type ultrasonication. After centrifugation, the upper layer (~75%) of the supernatant was subjected to UV−vis−NIR (Figure 2a) and CD measurements (Figure 1).

Supporting Information Available: Experimental details of the synthesis of (*R*)- and (*S*)-**1**, the absorption and the CD spectra to confirm complexation between SWNTs and **1**, and deconvoluted vis−NIR and Raman spectra. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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