Highlight Review

Optical Resolution of Single-Walled Carbon Nanotubes through Molecular Recognition with Chiral Diporphyrin Nanotweezers

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Abstract

Single-walled carbon nanotubes (SWNTs) have either chiral or achiral form, and synthesized chiral SWNTs include both left- and right-handed structures in equal amounts. Recently, a racemic mixture was found to be resolved through molecular recognition with gable-type chiral diporphyrins, namely, nano-tweezers. This novel separation method for SWNTs allowed optical resolution of SWNTs for the first time. The chiral nanotweezers consist of two chiral porphyrins and rigid spacer in between. Therefore, they have potential to discriminate not only the handedness but also the diameters or alignments of the hexagons of SWNTs. We have prepared the following three types of chiral nanotweezers; *m*-phenylene-, 2,6-pyridylene-, and 3,6-carbazolylene-bridged diporphyrins. In the extraction of SWNTs, different selectivities have been observed among the nanotweezers. This can be attributed to the differences in their structures; namely, the dihedral angles and the distance of the two porphyrins. In this review, we would like to discuss the relationship between the structures of the nanotweezers and the results of the optical and (*n*,*m*) enrichments of the extracted SWNTs.

Figure 1. (a) Armchair, (b) zigzag, and (c) chiral SWNTs. *M* and *P* describe the handedness and will be defined in Figure 2.

♦ Introduction

Carbon nanotubes (CNTs) have a cylindrical structure consisting of wrapped graphene sheets. The structures of CNTs are characterized by a variety of structural features.[1] The most characteristic is the number of layers which make up their cylindrical walls. Among CNTs, single-walled carbon nanotubes (SWNTs) have drawn the most steadfast attention because of their simple structures and properties.[2,3] The properties of SWNTs are largely dependent on the alignment of the hexagons as shown in Figure 1. For their electronic properties, the armchair SWNTs (Figure 1a) have metallic property, and zigzag (Figure 1b) and chiral varieties (Figure 1c) are either metallic or semiconducting depending on the roll-up index (*n*,*m*) (Figure 2). Although chiral SWNTs have potential to exhibit optical activity arising from enrichment of either left- or right-handed structure, optically active SWNTs have been elusive until our recent work.[4]

Since the electrical and optical properties of SWNTs are closely correlated to their structures as mentioned above, structural control of SWNTs is vital for application to nano-electronics and nanooptics.[5] Extensive investigations have been made in pursuit of selective synthesis and separation of SWNTs with specific structural or electrical properties. Although great
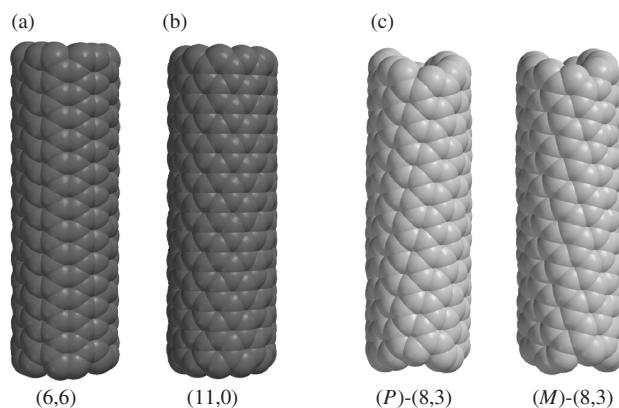
progress has been made recently on the selective synthesis of metallic and semiconducting SWNTs,[6,7] SWNTs have to be separated to obtain a specific (*n*,*m*) structure as a pure form.[8–13] The separation methods reported so far include density-gradient ultracentrifugation (DGU),[14–18] chromatography,[19–22] polymer-assisted selective extraction,[14,23–27] and electrochemical doping.[28–30] Relatively small molecules have also been applied to the separation of SWNTs through discrimination of a specific (*n*,*m*) structure.[23,24,31,32] In this review, we would like to introduce a novel method for the separation of SWNTs according to handedness through molecular recognition with gable-type chiral diporphyrins, developed recently in our group.[4,33–35]

♦ Structures of SWNTs

Since a SWNT can be visualized by curling a graphene sheet into a seamless cylinder, the structure is geometrically defined by a roll-up vector C_h given by two unit vectors a_1 and a_2; $C_h = na_1 + ma_2$, where *n* and *m* are integers and designated as the roll-up index (*n*,*m*) as shown in Figure 2a.[1,36] The (*n*,*m*) and C_h have been referred to as the chiral index (or simply chirality) and the chiral vector, respectively. However, the meaning of chiral in this context is different from the original meaning defined by the International Union of Pure and Applied Chemistry (IUPAC); that is, "the geometric properties of a rigid object of being nonsuperposable on its mirror image."[37] While

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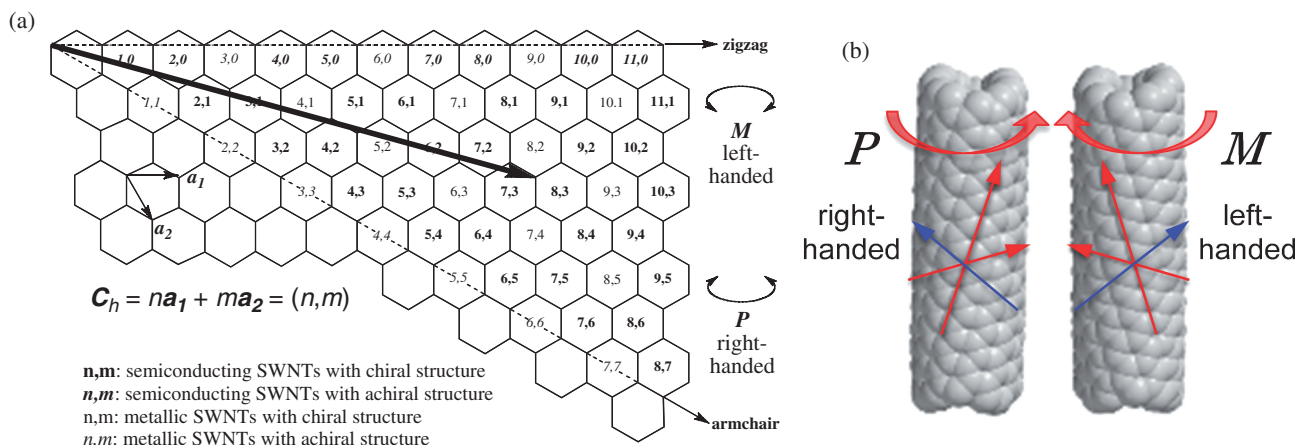E-mail: nkomatsu@belle.shiga-med.ac.jp

Figure 2. (a) (8,3)-SWNTs defined by rolling up the graphene map along the roll-up vector C_h indicated as the straight arrow in the map. The mirror-image structures, P and M, are visualized by rolling up the map from the front to the back, indicated as ⌣, and from the back to the front, indicated as ⌢, respectively. (b) Definition of P and M stereoisomers of (8,3)-SWNTs. Red and blue arrows are drawn along the zigzag structures.[1]

chiral SWNTs have nonsuperposable mirror-image structures shown in Figure 1c, armchair and zigzag structures do not have a nonsuperposable mirror image, which is achiral, as shown in Figures 1a and 1b. Whether a SWNT is chiral or achiral under the definition in chemistry, the terms of the chiral index, chirality, and chiral vector have been used to define its structure in this field. Since this terminology is confusing as Strano pointed out in his article,[38] an explicit nomenclature is required to define the structures of CNTs.[8]

For the expression of the stereoisomers of chiral SWNTs, a variety of terms have been used so far; *LH* and *RH*,[4] *r* and *l*,[39] *L* and *R*,[40] (n_1,n_2) and (n_2,n_1),[41] *ZL* and *ZR*,[1] and *AL* and *AR*.[1] Since stereochemistry of SWNTs have been discussed experimentally in several articles,[4,18,33–35,42] definite nomenclature is required for the stereochemistry of SWNTs.[38] In this paper, *M* and *P* terminology[4,8,33–35] is proposed to define left- and right-handed helical structures of SWNTs on the basis of the definition of *ZL* and *ZR* (Figure 2).[1] Since this terminology is easier to recognize in a space-filling model (Figure 2b), we adopt the terminology based not on *AL* and *AR* but on *ZL* and *ZR*.[1,4,33–35] The *M* and *P* terminology is authorized by the IUPAC for defining helical isomers; "The *chirality* of a helical, propeller, or screw-shaped molecular entity. A right-handed helix is described as *P* (or plus), a left-handed one as *M* (or minus)."[37]

♦ *Chiral Diporphyrin Nanotweezers*

For discrimination of stereoisomers of chiral SWNTs, we designed gable-type host molecules **1**–**3** (Scheme 1) consisting of two chiral porphyrins and rigid spacers in between. The host molecules are referred to as nanotweezers and were synthesized according to Scheme 1. The (*R*)- and (*S*)-monoporphyrins were prepared by the reaction of 2,2′-dipyrrylmethane with *N*-Boc-(*R*)- and (*S*)-phenylalaninals, respectively. After they were functionalized with a boronate group at the meso position, arene dihalides were reacted with the boronates via Suzuki–Miyaura coupling to give chiral diporphyrin nanotweezers **1**–**3**.[4,33–35]

Their structural features are summarized in Table 1. Molecular modeling indicates that the dihedral angles made by two porphyrins are made smaller by replacing the *m*-phenylene spacer in **1** with 2,6-pyridylene in **2**. Accordingly, the Zn–Zn distances of the two porphyrins become shorter. 3,6-Carbazolylene spacer in **3** also makes the dihedral angle smaller but the Zn–Zn distance longer because of the tricyclic structure of the spacer. The carbazolylene-bridged nanotweezers **3** have narrower dihedral angle and longer length of the spacer than the phenylene- and pyridylene-bridged nanotweezers **1** and **2**. These structural features of the nanotweezers largely affect the structures of SWNTs preferentially extracted, as will be discussed below.

♦ *Extraction of SWNTs with Chiral Nanotweezers*

In the extraction, CoMoCAT (SWNTs prepared by chemical vapor deposition (CVD) using a silica-supported Co–Mo catalyst) and nanotweezers in methanol was bath-sonicated and centrifuged. The nanotweezers have enough solubility in methanol to solubilize SWNTs after complexation. The formation of the complex was confirmed by red shifts in the absorption spectra, quenching of the fluorescence from the porphyrin, and enhanced Cotton effects in circular dichroism (CD) spectra.[43] After concentration of the supernatant, the diporphyrin was washed from the complex with pyridine and THF. The removal of the diporphyrin was confirmed by disappearance of the Soret band of the porphyrin in the washings. This process is important to obtain pristine SWNTs and avoid induced CD.[44] Since removal of the detergent and additives following the separation is considered not to be facile in other methods such as DGU and polymer wrapping, this washing process is one of the characteristics of our methodology as well as the flexibility in the molecular design of the host molecules mentioned above. The solid sample was subjected to Raman spectroscopy to compare the relative (n,m) abundance of SWNTs before and after the extraction. After dissolving in D_2O
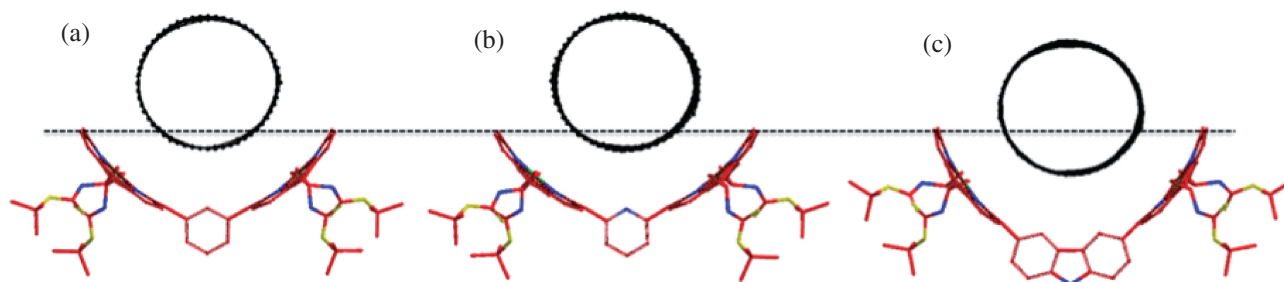
Scheme 1. Synthesis of chiral diporphyrin nanotweezers **1**–**3**.

Table 1. Structural features of the chiral nanotweezers **1**–**3**[a]

Compound	Dihedral angle[b] /degree	Zn–Zn distance[c] /nm
1	111	1.07
2	94	1.03
3	74	1.27

[a]Molecular mechanics calculation. [b]The angles made by two porphyrins. [c]The distance between two Zn metals of porphyrins.

with the aid of achiral detergent (sodium dodecylbenzene-sulfonate, SDBS), absorption and CD spectra were measured to evaluate the (*n*,*m*) and optical enrichments of SWNTs, respectively. Since the chiral nanotweezers can recognize both handedness and diameter or the alignment of the hexagons, we will discuss the enrichments of the (*n*,*m*) and optical purity of SWNTs in the following two sections consecutively.

Figure 3. (a) Absorption spectra of CoMoCAT and SWNTs extracted with **1**–**3** in near infrared region. (b) Raman spectra of CoMoCAT and SWNTs extracted with **2** and **3** in radial breathing mode at an excitation of 633 nm. (c) (*n*,*m*) Enrichments of SWNTs after the extraction with chiral nanotweezers **1**–**3**.

♦ (n,m) Enrichment

(*n*,*m*) Enrichment was qualitatively evaluated by absorption and Raman spectra as shown in Figures 3a and 3b, respectively.[19] In the absorption spectra, SWNTs extracted with **1** and **2** show similar spectra and, hence, the tweezers **1** and **2** exhibit

Figure 4. Computer-generated molecular modeling of the complex structures of (8,4)-SWNT with chiral nanotweezers **1** (a), **2** (b), and **3** (c). The dotted lines are drawn to clarify the depth of SWNT accepted in the cleft of the nanotweezers.

similar selectivity toward the (n,m) structures of SWNTs. (6,5) and (7,5), the two most abundant components in CoMoCAT, relatively decreased and instead (8,3), (8,4) and/or (7,6), and (9,1) increased after the extraction. Raman spectra show the relative increase of (9,4), (8,3), and (10,3), the relative decrease of (7,5), (6,5), and (6,4), and no clear change in (7,6), after the extraction with **2**. As shown in Figure 3c, we conclude that several structures, (8,3), (8,4), (9,4), (10,3), and (9,1), are enriched slightly through the extraction with **1** and **2**.

Although the (n,m) abundance seems not to differ much before and after extraction with **1** and **2**, the abundance was dramatically changed after extraction with **3**. In the absorption spectra (Figure 3a), (6,5) largely decreased, while (7,5) and (8,4) and/or (7,6) enriched clearly. Relative decrease of (6,5), (6,4), and (9,4) and increase of (7,6), (7,5), and (8,3) are observed in the Raman spectra (Figure 3b). From these spectra, we conclude that (7,6), (7,5), (8,4), and (8,3) are enriched after extraction with **3** as shown in Figure 3c.

In the map shown in Figure 3c, the enriched (n,m) through the extraction with nanotweezers **1** and **2** distributes in a wide range of the roll-up angles (5–19°) and diameters (0.76–0.94 nm). This indicates that the extraction with **1** and **2** is not so selective in terms of (n,m). On the other hand, the (n,m) enriched by **3** also possesses a wide range of roll-up angles (15–27°) but narrower diameter range (0.78–0.89 nm). This shows that **3** recognized the diameter of the SWNTs rather than roll-up angle.[34]

The selectivity difference between the employed nanotweezers, mentioned above, can be accounted for by computer-generated complex structures, depicted in Figure 4. The nanotweezers **3** have a smaller dihedral angle (74°) and a longer Zn–Zn distance (1.27 nm), as compared with **1** and **2** that have dihedral angles of 111 and 94° and the Zn–Zn distances of 1.07 and 1.03 nm, respectively, as shown in Table 1. Such structural characteristics of **3** allow much deeper accommodation of a SWNT as shown in Figure 4c, enabling precise differentiation of the diameter. On the other hand, shallower contacts are only possible for **1** and **2** as shown in Figures 4a and 4b, making the recognition of diameter very difficult and giving less selectivity. Since the SWNTs extracted with **3** still include a few kinds of (n,m) structures, we are modifying the structure of nanotweezers for further improvement of the (n,m) selectivity as well as the optical enrichment.[45]

♦ *Optical Enrichment*

The nanotweezers also have the ability to discriminate the

handedness of SWNTs, M and P structures defined above, other than the (n,m) structures, as mentioned above. The optical activity originating from the SWNTs was confirmed by measurement of the CD of the extracted SWNTs. Before measuring the CD, it was necessary to thoroughly remove the chiral diporphyrins to avoid induced CD.[44]

When the first designed nanotweezers **1** were applied to the extraction of CoMoCAT, at least two major components in the extract, (6,5) and (8,4), exhibited CDs as shown in Figure 5a. The CD spectra of the SWNTs extracted with (R)- and (S)-**1** are symmetric and opposite,[4] and the CD signs from each (n,m) are alternate in the E^S_{33} and E^S_{22} regions (electronic transitions parallel to the nanotube axis in semiconducting SWNTs).[46] For example, the CDs corresponding to (6,5)-SWNTs are observed at 341 and 562 nm as shown in Figures 5a and 5b. (6,5)-SWNTs extracted with (R)-**1** and -**2** exhibit (+, −) alternate signs at 341 and 562 nm, while those extracted with the corresponding (S)-stereoisomers show (−, +) signs at the same wavelengths. These alternate features of CD are consistent with the theoretical prediction,[1,36,47,48] hence, indicating optical activities of the extracted SWNTs.[4]

The second nanotweezers **2**, with narrower dihedral angle and slightly shorter Zn–Zn distance shown in Table 1 and Figure 4, enhanced the optical enrichment of (6,5)-SWNTs (Figure 5b). SWNTs extracted by **1** show two prominent CD peaks at 341 and 562 nm corresponding to E^S_{33} and E^S_{22} transitions of the (6,5)-SWNTs, respectively.[19,49] The extracted SWNTs other than (6,5) showed much lower intensity CD. These spectral features suggest much higher discrimination ability of **2** to the handedness of (6,5)-SWNTs,[33] although the optical purity cannot be determined quantitatively.[45] In the extraction of CoMoCAT with **2**, the abundance of (6,5)-SWNTs was relatively decreased after the extraction as discussed above. However, the extracted (6,5)-SWNTs possess higher optical activity than other extracted SWNTs. These results show that the (n,m) and optical enrichments are achieved through recognition of the diameter and handedness of SWNTs independently by the shape of the cleft (Figure 4) and the stereogenic center at the periphery of the porphyrins (Scheme 1) in the nanotweezers, respectively. In order to obtain only one enantiomer of SWNTs with high purity, simultaneous enrichments of the optical purity and the (n,m) abundance are required in a specific (n,m)-SWNTs. Therefore, we designed the latest nanotweezers **3** and applied it to the selective extraction of CoMoCAT.

In the CD spectra shown in Figure 5c, SWNTs extracted with (R)- and (S)-**3** also provide symmetric and opposite CD
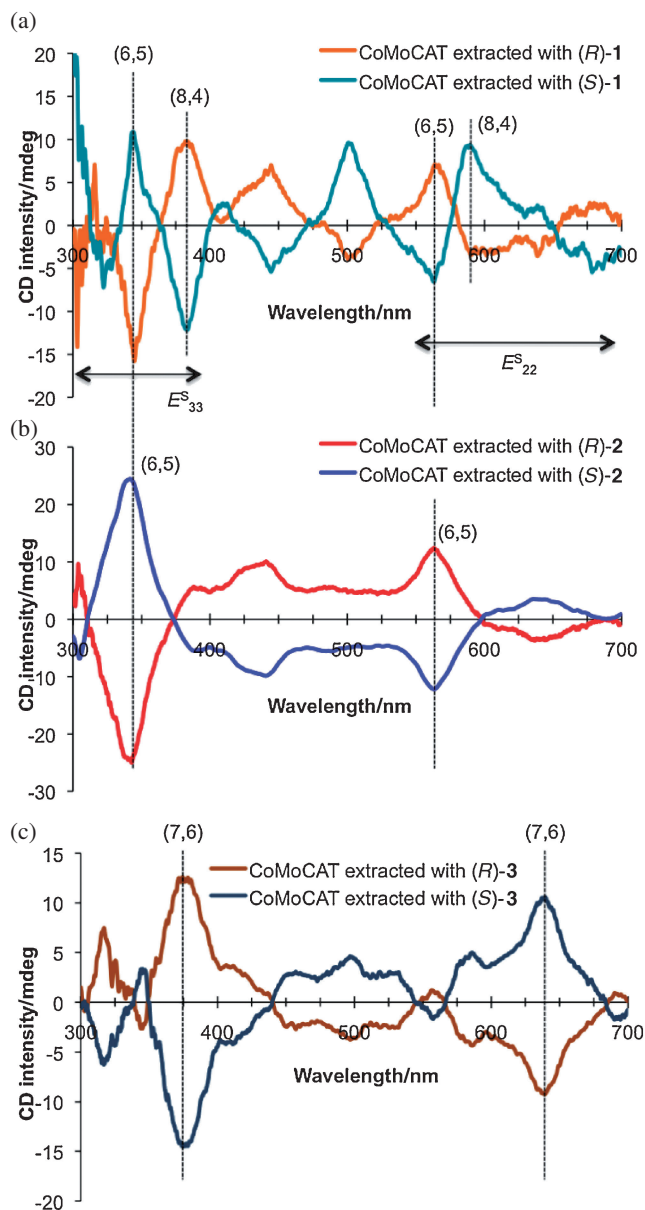
Figure 5. CD spectra of SWNTs extracted with (*R*)- and (*S*)-**1** (a), (*R*)- and (*S*)-**2** (b), and (*R*)- and (*S*)-**3** (c) in visible region.

signals, indicating that the two stereoisomers of **3**, *R* and *S*, preferentially extracted SWNTs with different helicities, *M* and *P*, 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 (7,6)-SWNTs, respectively. (7,5)-SWNTs were thought to be optically enriched because they are one of the most abundant components in CoMoCAT, enriched through the extraction with **3** as discussed above, and have very close absorption wavelength in the E^S_{22} region to that of (7,6)-SWNTs.[34] Recent reports regarding the isolation and characterization of a number of (*n,m*)-SWNTs reveal that the optically enriched (*n,m*) here is thought not to be (7,5) but (7,6).[19,49] This indicates that the handedness in (7,6)-SWNTs was selectively discriminated by **3**, while other (*n,m*)-SWNTs were not optically enriched as much. Because (7,6) is one of the (*n,m*)-enriched

SWNTs, one enantiomer of (7,6) increases in purity through the extraction with **3**. This indicates that we made progress toward our goal to obtain single structures of SWNTs consisting of one enantiomer of a specific (*n,m*) by tuning the structure of the nanotweezers.

Upon the extraction with **2**, (6,5)-SWNTs were optically enriched much more than other (*n,m*)-SWNTs.[33] Although the structures of (7,6) and (6,5) are not so different in terms of diameters (0.13 nm difference) and roll-up angles (0.5 degree difference) as shown in Figure 3c, the most optically enriched SWNTs were changed from (6,5) to (7,6) by just changing the spacer from pyridylene to carbazolylene. This indicates that nanotweezers can differentiate subtle structural differences between SWNTs. The changes in the structure of the nano-tweezers influence the structure of SWNTs extracted preferentially.[33]

♦ *Concluding Remarks*

The concept of our research is to apply methodologies in organic chemistry to nanocarbon materials, especially CNTs and nanodiamonds (NDs). Organic chemistry deals with organic molecules. Although their sizes are different significantly from those of nanocarbon materials, both of them are composed mainly of carbon atoms. This similarity provides organic characteristics to nanocarbon materials, which are categorized as inorganic rather than organic. For example, many organic reactions have been applied to CNTs and NDs to bind organic functionalities on their surfaces through covalent bonds.[50–53] Since nanomaterials have large specific surface area, their physical properties can be controlled by dense coverage of the surface with desired functional groups. We are trying to treat CNTs and NDs as organic molecules. In other words, we are trying to enlarge the field of organic chemistry from conventional organic molecules to newly found nanocarbon materials.

ND chemistry conducted in our group is based on synthetic organic chemistry. We performed multistep organic transformations on the surface of ND and characterized the added and transformed functionalities mainly by solution-phase NMR techniques in each step.[54–56] The functionalized NDs were successfully dissolved into not only pure water but also buffer solution. After adding more functions such as targeting specificity and imaging modalities, we will apply the functionalized NDs to biological entities as imaging probes.

The separation of SWNTs presented here is based on supramolecular chemistry. Although several methods have been reported for the separation of SWNTs, this method is quite unique. An advantage of our method lies in the flexibility in the molecular design of the host molecules, which gives us infinite possibilities. This is in marked contrast with most other work using commercially available compounds for separating SWNTs. The final destination of this research is to obtain single structure SWNTs consisting of one enantiomer of a specific (*n,m*). To fulfill our goal, we continue to revise the host molecule by taking into account the results of the optical and (*n,m*) selectivities we obtained.[45] We believe that we can achieve this in the near future by fully utilizing our knowledge and experience in the fields of synthetic organic, supramolecular, and materials chemistry.

References and Notes

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