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REVIEW ARTICLE

Separation of nanocarbons by molecular recognition

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Abstract This review article surveys the author's work during the last ten years. The research works have been carried out in the interdisciplinary fields of supramolecular, synthetic organic and materials chemistry. This review consists of the following 5 topics; (1) novel synthetic methodology for constructing benzyl ether-linked oxacyclophanes and oxacalixarenes by reductive coupling reactions, (2) preferential precipitation of C_{70} over C_{60} with *p*-halohomooxacalix[3]arenes prepared by the above reductive coupling reactions, (3) highly practical purification of fullerenes by filtration through activated carbon thin layer, (4) host-guest chemistry of C_{60} and C_{70} with porphyrin monomers and dimers in solution, and (5) optical resolution of carbon nanotubes through preferential complexation with chiral diporphyrin nanotweezers. New terminology is also proposed in the definition of the structures and stereochemistry of carbon nanotubes.

Keywords Carbon nanotubes · Fullerenes · Materials chemistry · Supramolecular chemistry · Synthetic chemistry

Abbreviations

AC	Activated carbon
Bn	Benzyl
CD	Circular dichroism
CNT	Carbon nanotube
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DWNT	Double-walled carbon nanotube
GPC	Gel permeation chromatography
HRTEM	High-resolution transmission electron microscopy
MWNT	Multi-walled carbon nanotube
Oct^t	1,1,3,3-Tetramethylbutyl
SWNT	Single-walled carbon nanotube
SDBS	Sodium dodecylbenzenesulfonate
TMB	1,2,4-Trimethylbenzene

Introduction

Fullerenes were discovered by Kroto, Smalley et al. in 1985 [1] and first synthesized in macroscopic quantity by Krätschmer, Huffman et al. in 1990 [2]. On the other hand, DWNTs and MWNTs were found by Iijima in 1991 [3], though it is somewhat controversial [4–8]. SWNTs were first prepared independently by Iijima et al. [9] and Bethune et al. in 1993 [10]. Both fullerenes and CNTs belong to the third allotrope of carbon following diamond and graphite and are referred to as nanocarbons (or nanocarbon compounds, nanocarbon materials). However, some physical properties, in particular their solubilities, are remarkably different; fullerenes are soluble in some organic solvents, and CNTs show no solubility to any solvents. Owing to the contrastive behaviors, different strategies were employed for purification of these compounds in principle. Actually, we precipitated C_{70} preferentially from a toluene solution of C_{60} and C_{70} mixture to enhance the purity of C_{70} [11, 12], passed a solution of fullerene mixture through AC thin layer to obtain pure C_{60} and C_{70} [13, 14] and investigated the complexation of C_{60} and C_{70} with porphyrins in a solution [15, 16, 17, 18]. Since a similar method was not applicable to CNT separation because of their poor solubility, we used supramolecular strategy in a sense contrary to that of the

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preferential precipitation of C_{70}. That is, insoluble CNTs were solubilized by complexation with a host molecule, making it possible to extract the CNT of the desired morphology through molecular recognition. Indeed, we successfully obtained optically active SWNTs for the first time by preferential extraction of SWNTs into methanol by complexation with chiral gable-type porphyrin dimers [19–21].

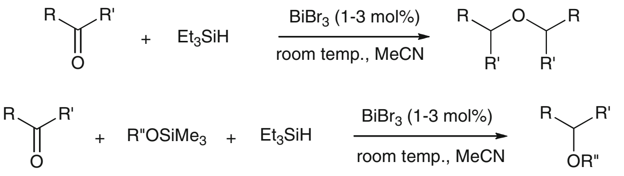
On the other hand, it is well-known that physical properties such as electrical and optical ones of nanocarbons are largely dependent on their structures [22]. Therefore, separation of nanocarbons are of great importance and demand in view of fundamental studies and technological applications [23]. The concept of our research in nanocarbon chemistry is "control of the physical properties by control of the chemical structures". We have been trying to achieve it by supramolecular strategies.

This review highlights the author's work during the last 10 years. His work related to the supramolecular chemistry began with a small finding of a novel ether forming reaction [24] encountered during the exploration of bismuth salt-catalyzed organic reactions [25–30]. The new methodology was extended to synthesis of macrocycles tethered by benzylic ethers [11, 31], which was applied to fullerene separation [12]. After practical separation of fullerenes was developed [13, 14, 32], investigations on the host-guest interaction between fullerenes and porphyrins [15–18] started under influence of Prof. Osuka (Kyoto University), which led to the successful separation of CNTs according to their structures by the use of diporphyrin nanotweezers [19–21].

New synthetic route to homooxacalix[*n*]arenes via reductive coupling reactions

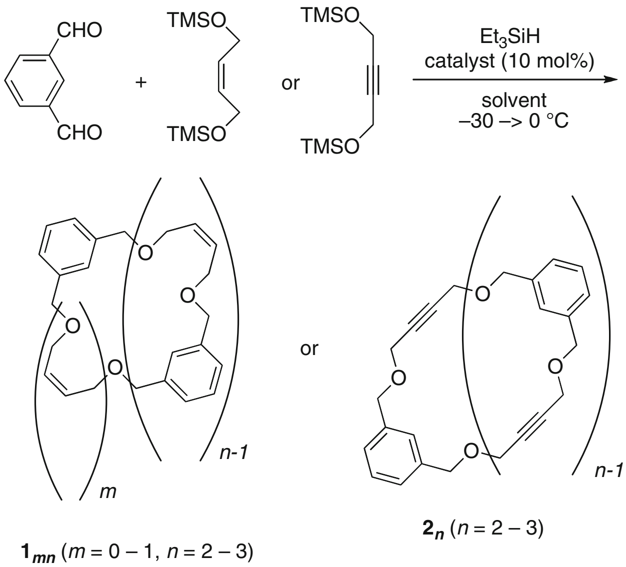
In 1997, we found bismuth bromide-catalyzed reductive coupling reactions as shown in Scheme 1 [24]. The ether forming reactions proceeded under neutral conditions in the presence of a catalytic amount of bismuth bromide [30], which worked more efficiently than other catalysts reported so far [33–36]. Since such mild conditions are favorable for constructing labile linkages such as dibenzyl ethers, we applied these reactions to the synthesis of macrocyclic molecules with dibenzyl ether linkages such as oxacyclophanes and oxacalixarenes. In the cyclization, the bismuth salt was expected to work as a template [37, 38].

Oxacyclophanes represent an important class of host molecules due to the dual characteristics of cyclophanes and crown ethers. Among them, homooxacalix[*n*]arenes are the most promising receptors following calixarenes. Actually, hexahomotrioxacalix[3]arenes [11, 31, 39–41] and octahomotetraoxacalix[4]arenes [41–43] with or without *O*-protection exhibit characteristic affinities for alkali and alkaline-earth metal cations [44–46], ammonium ions [42, 46–51], lanthanide ions [52, 53], and fullerenes [11, 12, 39, 40, 41, 54–60]. They were also applied to the construction of biological models [61, 62] and supramolecular capsules [63–65]. However, their synthesis has been limited to the following two routes; (1) direct synthesis by dehydration of 2,5-bis(hydroxymethyl)phenols in the presence or absence of Brønsted acid at high temperature [40, 41, 55, 66–69], and (2) stepwise synthesis via acid-catalyzed cyclization of linear trimers [39] and condensation of a dimer and a monomer [70]. Therefore, the reductive coupling reaction of diformylphenols provides a novel synthetic route to homooxacalix[*n*]arenes [11, 12]. Since the reductive coupling reactions proceed under milder conditions, this route gave better yields of the cyclic products in a more facile procedure [11]. In addition, the separation of cyclic trimers and tetramers was easily achieved by simple filtration in most cases.



Scheme 1 Bismuth bromide-catalyzed reductive coupling reactions to form ether linkage under neutral conditions

First we carried out heterocoupling reactions of isophthalaldehyde with bis(trimethylsilyl) ethers of (*Z*)-2-butene-1,4-diol and 2-butyne-1,4-diol as shown in Scheme 2 [24].



1$_{mn}$ ($m = 0 - 1$, $n = 2 - 3$)

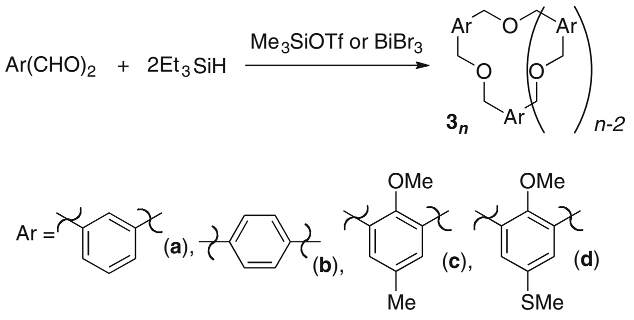
2$_n$ ($n = 2 - 3$)

Scheme 2 Synthesis of metacyclophanes with olefinic ether linkages via reductive heterocoupling reactions

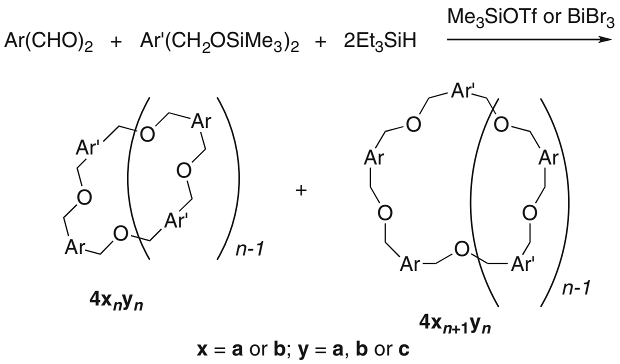
GPC separation gave pure $\mathbf{1_{12}}$ and $\mathbf{2_2}$ as major cyclic products and $\mathbf{1_{02}}$, $\mathbf{1_{03}}$, $\mathbf{1_{13}}$ and $\mathbf{2_3}$ as minor ones.

Much larger macrocycles up to 77-membered ring were obtained by reductive homocoupling of arenedialdehydes as shown in Scheme 3 [31]. Series of macrocycles obtained by the reactions were isolated by GPC to give pure oxa[3.$_n$]metacyclophanes ($\mathbf{3a}_n$, $n = 3$–8), oxa[3.$_n$]paracyclophanes ($\mathbf{3b}_n$, $n = 4$–11), *p*-methylhomooxacalix[*n*]arenes ($\mathbf{3c}_n$, $n = 3$–9) and *p*-(methylthio)homooxacalix[*n*]arenes ($\mathbf{3d}_n$, $n = 4$–7). The reductive heterocoupling of arenedialdehydes and bis(trimethylsilyloxymethyl)benzenes shown in Scheme 4 provided a series of macrocyclic ethers consisting of not only even numbers of the aromatics ($\mathbf{4a}_n\mathbf{a}_n$ (= $\mathbf{3a}_{2n}$), $\mathbf{4b}_n\mathbf{b}_n$ (= $\mathbf{3b}_{2n}$), $\mathbf{4a}_n\mathbf{c}_n$ and $\mathbf{4b}_n\mathbf{c}_n$) but also odd numbers ($\mathbf{4a}_{n+1}\mathbf{a}_n$ (= $\mathbf{3a}_{2n+1}$), $\mathbf{4b}_{n+1}\mathbf{b}_n$ (= $\mathbf{3b}_{2n+1}$), $\mathbf{4a}_n\mathbf{c}_{n+1}$ and $\mathbf{4b}_n\mathbf{c}_{n+1}$) [31]. Novel macrocyclic ethers hybridized homooxacalix[*n*]arene with oxacyclophane ($\mathbf{4a}_n\mathbf{c}_n$, $\mathbf{4a}_n\mathbf{c}_{n+1}$, $\mathbf{4b}_n\mathbf{c}_n$ and $\mathbf{4b}_n\mathbf{c}_{n+1}$) were also prepared by the heterocoupling reaction.

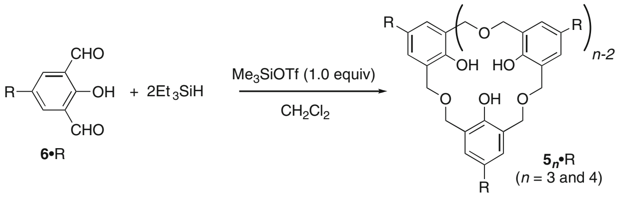
Although the above coupling reactions were limited to be employed in the synthesis of methyl-protected homooxacalix[*n*]arenes ($\mathbf{3c}_n$ and $\mathbf{3d}_n$ in Schemes 3, and $\mathbf{4a}_n\mathbf{c}_n$, $\mathbf{4a}_n\mathbf{c}_{n+1}$, $\mathbf{4b}_n\mathbf{c}_n$ and $\mathbf{4b}_n\mathbf{c}_{n+1}$ in Scheme 4), the homocoupling reaction of diformylphenols ($\mathbf{6}\cdot$R) was found to proceed in the presence of a stoichiometric amount of Me_3SiOTf at lower temperature, −78 to 0 °C, giving homooxacalix[*n*]arenes ($\mathbf{5}_n\cdot$R, $n = 3$ and 4) as shown in Scheme 5 [11, 13]. In contrast to the synthesis of methyl-protected homooxacalix[*n*]arenes ($\mathbf{3c}_n$ and $\mathbf{3d}_n$), the $\mathbf{5}_3\cdot$R and $\mathbf{5}_4\cdot$R were exclusively obtained as cyclic products regardless of the R-substituents. This is probably due to hydrogen bonding between the phenolic hydroxy groups; hydrogen bonding network in the linear trimer and tetramer would facilitate their cyclization to give $\mathbf{5}_3\cdot$R and $\mathbf{5}_4\cdot$R in good yields (Table 1), while linear precursors larger than tetramer could not adopt a conformation suitable for cyclization.



Scheme 3 Serial synthesis of oxa[3.$_n$]cyclophanes and homooxacalix[*n*]arenes via reductive homocoupling of arenedialdehydes



Scheme 4 Serial synthesis of oxa[3.$_n$]cyclophanes ($\mathbf{4a}_n\mathbf{a}_n$ (= $\mathbf{3a}_{2n}$), $\mathbf{4a}_n\mathbf{a}_{n+1}$ (= $\mathbf{3a}_{2n+1}$), $\mathbf{4b}_n\mathbf{b}_n$ (= $\mathbf{3b}_{2n}$) and $\mathbf{4b}_n\mathbf{b}_{n+1}$ (= $\mathbf{3b}_{2n+1}$)) and homooxacalix[*n*]arenes ($\mathbf{4a}_n\mathbf{c}_n$, $\mathbf{4a}_n\mathbf{c}_{n+1}$, $\mathbf{4b}_n\mathbf{c}_n$ and $\mathbf{4b}_n\mathbf{c}_{n+1}$) via reductive heterocoupling of arenedialdehydes and bis(trimethylsilyloxymethyl)benzenes. The notations (**a**–**c**) for the structures of the aromatic units (Ar and Ar′) are shown in Scheme 3



Scheme 5 Synthesis of homooxacalix[*n*]arenes ($\mathbf{5}_n\cdot$R, $n = 3$ and 4) by reductive homocoupling reaction of 4-substituted-2,5-diformylphenols ($\mathbf{6}\cdot$R)

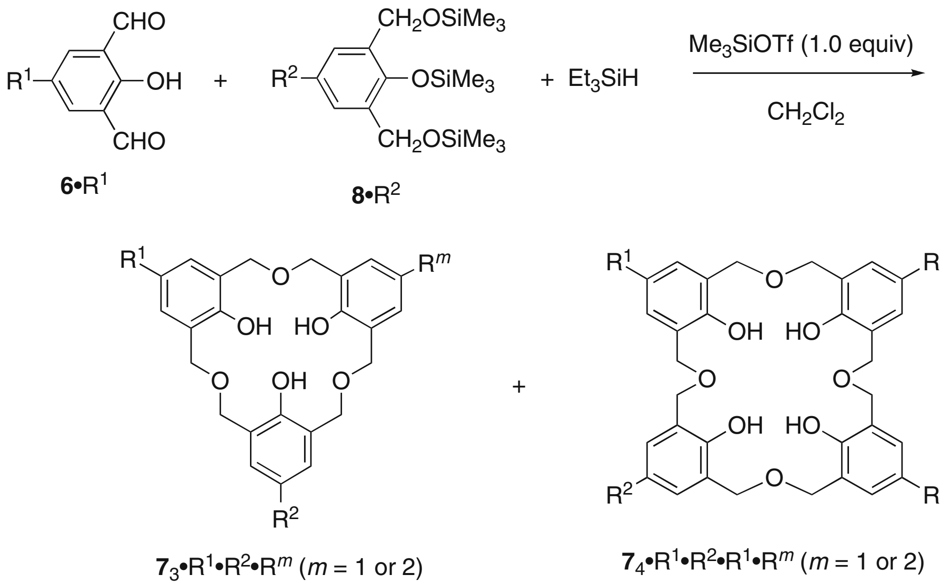
Table 1 Synthesis of homooxacalix[*n*]arenes ($\mathbf{5}_n\cdot$ R; $n = 3$, 4) by reductive homocoupling reaction in the presence of Et_3SiH (2.0 equiv.) and Me_3SiOTf (1.0 equiv.) in CH_2Cl_2

Run	R	Concentration (M)	React. time (h)	Temp (°C)	Yield (%)[a]	
					$\mathbf{1_3}$	$\mathbf{1_4}$[b]
1	*t*-Bu	0.05	8	−78	38	22
2	Me	0.05	7.5	−78	35	12
3	Bn	0.05	7.5	−78	32	14
4	Ph	0.05	9.5	−45	11	18
5	F	0.01	9	0	29	24
6	Cl	0.01	7	0	29	22
7	Br	0.01	7.5	0	28	26
8	I	0.01	9	0	13	0

[a] Isolated yield

[b] Separated as white solid insoluble in ethyl acetate except for $\mathbf{5}_4\cdot$ *t*-Bu in run 1

Heterocoupling reaction of $\mathbf{6}\cdot R^1$ with $\mathbf{8}\cdot R^2$ also provided homooxacalix[*n*]arenes ($n = 3$ and 4) exclusively in good yields at −78 °C (Scheme 6) [11]. The stoichiometry of the $\mathbf{6}\cdot R^1$ and $\mathbf{8}\cdot R^2$ was found to control the distribution of the cyclic products, $\mathbf{7}_3\cdot R^1\cdot R^2\cdot R^m$ ($m = 1$ or 2) and $\mathbf{7}_4\cdot R^1\cdot R^2\cdot R^1\cdot R^m$ ($m = 1$ or 2). The results are summarized in Table 2. The products were separated by filtration and column chromatography using a similar procedure to that used in the homocoupling reaction. An



Scheme 6 Synthesis of homooxacalix[*n*]arenes ($\mathbf{7_3} \cdot R^1 \cdot R^2 \cdot R^m$ and $\mathbf{7_4} \cdot R^1 \cdot R^2 \cdot R^1 \cdot R^m$, $m = 1$ or 2) with various substituents on their upper rims by reductive heterocoupling reaction of 2,5-diformylphenols ($\mathbf{6} \cdot R^1$) with TMS ethers ($\mathbf{8} \cdot R^2$)

equimolar reaction between $\mathbf{6} \cdot R^1$ and $\mathbf{8} \cdot R^2$ gave $\mathbf{7}_4 \cdot R^1 \cdot R^2 \cdot R^1 \cdot R^2$ preferentially (runs 1–7). When the *p*-substituents, R^1 and R^2, are the same, $\mathbf{5}_4$ was obtained as a major product (run 4). When the ratio of $\mathbf{6} \cdot$ F and $\mathbf{8} \cdot$ *t*-Bu was changed to 2:1 and 3:1 in runs 8 and 9, $\mathbf{7}_3 \cdot$ F $\cdot$ *t*-Bu $\cdot$ F and $\mathbf{7}_4 \cdot$ F $\cdot$ *t*-Bu $\cdot$ F $\cdot$ F were produced as the major products, respectively. Although $\mathbf{7}_3 \cdot$ F $\cdot$ *t*-Bu $\cdot$ *t*-Bu was not obtained in run 8, the use of the substrates with the reversed substituents, $\mathbf{6} \cdot$ *t*-Bu and $\mathbf{8} \cdot$ F, in a 2:1 ratio provided $\mathbf{7}_3 \cdot$ *t*-Bu $\cdot$ F $\cdot$ *t*-Bu (=$\mathbf{7}_3 \cdot$ F $\cdot$ *t*-Bu $\cdot$ *t*-Bu) as a major product (run 10). This method realized the preferential preparation of all the homooxacalix[*n*]arenes ($n = 3$ and 4) with one or two kinds of substituents, except one homooxacalix[4]arene ($\mathbf{7}_4 \cdot R^1 \cdot R^1 \cdot R^2 \cdot R^2$), by choosing the reaction mode, the substrates and their stoichiometry, as shown in Fig. 1 [11].

Preferential precipitation of C_{70} with *p*-halohomooxacalix[3]arenes

Since the 1990s encapsulation of fullerenes has been a subject of interest in the fields of supramolecular and fullerene chemistry [71–78]. A practical goal of the chemistry is to develop an efficient method for the separation of specific size and/or isomer of fullerenes from the mixture [79]. To achieve this goal, selective complexation of fullerenes has been reported so far with calixarenes [11, 12,

Table 2 Synthesis of homooxacalix[*n*]arenes ($\mathbf{7}_3 \cdot R^1 \cdot R^2 \cdot R^m$ and $\mathbf{7}_4 \cdot R^1 \cdot R^2 \cdot R^1 \cdot R^m$, $m = 1, 2$) by reductive heterocoupling at −78 °C

Run	R^1 (mmol)[a]	R^2 (mmol)[a]	React. time (h)	Yield (%)[b]			
				$\mathbf{7}_3 \cdot R^1 \cdot R^2 \cdot R^1$	$\mathbf{7}_3 \cdot R^1 \cdot R^2 \cdot R^2$	$\mathbf{7}_4 \cdot R^1 \cdot R^2 \cdot R^1 \cdot R^1$	$\mathbf{7}_4 \cdot R^1 \cdot R^2 \cdot R^1 \cdot R^{2c}$
1	*t*-Bu (0.20)	Me (0.19)	8	8	5	0	28
2	Me (0.21)	*t*-Bu (0.20)	8	19	12	0	32
3	Bn (0.20)	*t*-Bu (0.20)	8	15	8	0	26
4	*t*-Bu (0.20)	*t*-Bu (0.21)	8	26 ($\mathbf{5}_3 \cdot$ *t*-Bu)		42 ($\mathbf{5}_4 \cdot$ *t*-Bu)	
5	Cl (0.20)	*t*-Bu (0.20)	11.5	5	7	0	20
6	Br (0.20)	*t*-Bu (0.20)	11.5	8	6	0	13
7	F (0.20)	*t*-Bu (0.20)	10	3	1	0	26
8	F (0.42)	*t*-Bu (0.20)	7.5	24	0	12	3
9	F (0.32)	*t*-Bu (0.11)	7	15	Trace	20	0
10[d]	*t*-Bu (0.43)	F (0.22)	7	22	0	13	8

[a] Amounts of $\mathbf{6} \cdot R^1$ and $\mathbf{8} \cdot R^2$ used are indicated in parentheses

[b] Isolated yield

[c] Separated as white solid insoluble in ethyl acetate except for $\mathbf{5}_4 \cdot$ *t*-Bu in run 4 and $\mathbf{7}_4 \cdot R^1 \cdot R^2 \cdot R^1 \cdot R^2$ in runs 1–3

[d] $\mathbf{5}_3 \cdot$ *t*-Bu was obtained in 13% yield

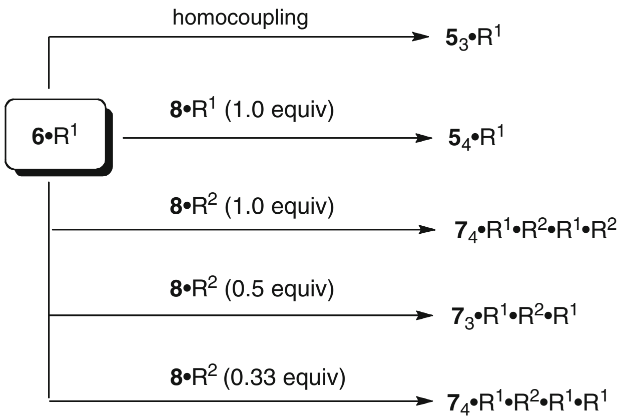
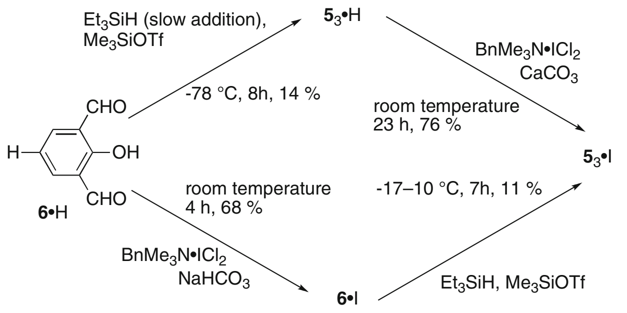


Fig. 1 Preferential preparation of homooxacalix[*n*]arenes ($\mathbf{5}_n$ and $\mathbf{7}_n$, $n = 3$ and 4) with various substituents on their upper rims

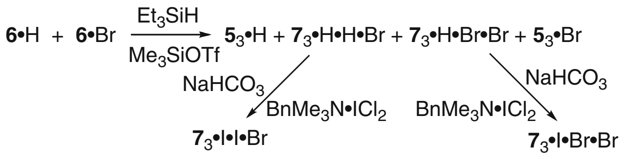
71, 73, 75, 76–78, 80–93], cyclodextrins [74, 76, 78, 80, 86, 94–108], cyclotriveratrylenes [76, 109–112], carbon nanorings [113–118] and porphyrins [15, 16, 72, 119–127]. In 1992, selective extraction of C_{60} into water layer was accomplished using γ-cyclodextrin [108] and water soluble calix[8]arene [93] by Wennerström et al. and Verhoeven et al., respectively. Selective precipitation from organic solution of fullerene mixture, which is more practical method aiming at the separation of fullerenes, was reported in 1994 using *p-tert*-butylcalix[8]arene [90, 91] and cyclotriveratrylenes [112] by Shinkai et al. and Atwood et al. More recently, a few bridged or cyclic dimers were found to encapsulate C_{70} preferentially to C_{60} in a solution [85, 88, 110, 126]. However, no host molecules precipitating C_{70} preferentially have been reported except for one example using *p-tert*-butylcalix[6]arene [87, 91].

With various kinds of homooxacalix[*n*]arenes ($n = 3$ and 4) in hand as mentioned above, we investigated their inclusion properties for fullerenes [11–13]. Although it was already known that homooxacalix[3]arenes and their dimers form stable complexes with C_{60} in solutions [54, 56–58, 60, 65, 84], we obtained more attractive result that *p*-halohomooxacalix[3]arenes preferentially precipitate C_{70} from solutions [12].

Various kinds of mono-, di- and triiodohomooxacalix[*n*]arenes ($n = 3$ and 4; $\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{R} \cdot \mathrm{R}$, $\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{R}$, $\mathbf{5}_3 \cdot \mathrm{I}$ and $\mathbf{7}_4 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{R}$) were prepared by reductive coupling reactions mentioned above [11, 12]. *p*-Triiodohomooxacalix[3]arene ($\mathbf{5}_3 \cdot \mathrm{I}$) was prepared stepwise from 2,6-diformylphenol ($\mathbf{6} \cdot \mathrm{H}$) [128] by a combination of iodination [129, 130] followed by reductive coupling [12] or by their reversed sequence (Scheme 7), because the diformylation of *p*-iodophenol [131] gave $\mathbf{6} \cdot \mathrm{I}$ in very low yield. *p*-Trihalohomooxacalix[3]arenes with different halogens, $\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{Br}$ and $\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{Br} \cdot \mathrm{Br}$, were prepared through the iodination [130] of the corresponding $\mathbf{7}_3 \cdot \mathrm{H} \cdot \mathrm{H} \cdot \mathrm{Br}$ and $\mathbf{7}_3 \cdot \mathrm{H} \cdot \mathrm{Br} \cdot \mathrm{Br}$ as shown in Scheme 8 [12]. Other *p*-halohomooxacalix[*n*]arenes with different substituents, $\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{Bn}$, $\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{Bn} \cdot \mathrm{Bn}$, $\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{Oct}^t$ and $\mathbf{7}_4 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{Oct}^t$, were prepared by the reductive heterocoupling reaction between 4-substituted-2,6-diformylphenol ($\mathbf{6} \cdot \mathrm{R}^1$) and tris(trimethylsilyl) ether of 4-substituted-2,6-bis(hydroxymethyl)phenol ($\mathbf{8} \cdot \mathrm{R}^2$) as shown in Scheme 6 [11, 12].



Scheme 7 Synthesis of *p*-iodohomooxacalix[3]arene ($\mathbf{5}_3 \cdot \mathrm{I}$) by the combination of iodination and reductive homocoupling



Scheme 8 Synthesis of *p*-bromoiodohomooxacalix[3]arenes ($\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{Br}$ and $\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{Br} \cdot \mathrm{Br}$) by reductive coupling of $\mathbf{6} \cdot \mathrm{H}$ and $\mathbf{6} \cdot \mathrm{Br}$ followed by iodination

Homooxacalix[*n*]arenes with a variety of *para*-substituents thus prepared were subjected to precipitation experiments of C_{70} (Table 3) [12]. About 70% of C_{70} was precipitated by $\mathbf{5}_3 \cdot \mathrm{I}$ from a toluene solution of C_{70} ($\sim$1 mg/mL) as a complex (runs 1 and 2). Under similar conditions, however, no precipitate was observed for C_{60} with $\mathbf{5}_3 \cdot \mathrm{I}$ (run 3). These contrastive results clearly show a potential of $\mathbf{5}_3 \cdot \mathrm{I}$ for separation of C_{70} from a mixture. The number of alkyl groups and kind of halogens at the *para* position in *p*-halohomooxacalix[*n*]arenes ($n = 3$ and 4) remarkably affected the yield of C_{70} (runs 4–9). *p*-Iodohomooxacalix[*n*]arenes ($n = 3$ and 4) with one alkyl group afforded C_{70} precipitate in low yields (runs 4–6), while only a trace amount of precipitate was obtained with *p*-iodohomooxacalix[3]arene having two alkyl groups (runs 7–8). *p*-Tribromohomooxacalix[3]arene ($\mathbf{5}_3 \cdot \mathrm{Br}$) gave C_{70} complex in 33% yield (run 9), which is less than a half of the yield with $\mathbf{5}_3 \cdot \mathrm{I}$ (runs 1 and 2). Similar precipitation from more concentrated toluene solution of C_{70} (2.5 mg/mL) has been carried out with *p-tert*-butylcalix[6]arene to give C_{70} complex in 31% yield [91].

Selective precipitation of C_{70} from a mixture of C_{60} and C_{70} was carried out under more concentrated conditions than those in Table 3 [132]. The results are summarized in

Table 3 Precipitation of C_{70} with *p*-halohomooxacalix[*n*]arenes ($\mathbf{5}_3$, $\mathbf{7}_3$ and $\mathbf{7}_4$) with various substituents[a]

Run	Host	Weight (mg) (μmol)	C_{70} (mg) (μmol)	Toluene (mL)	Precipitate	
					Weight (mg)	Yield (%) off C_{70}^{b}
1	$\mathbf{5}_3 \cdot \mathrm{I}$	24.1 (31)	51.3 (61)	48	52.5	71
2	$\mathbf{5}_3 \cdot \mathrm{I}$	52.8 (67)	111.6 (130)	96	109.2	67
3	$\mathbf{5}_3 \cdot \mathrm{I}$	4.3 (5.5)	3.8 (5.3)[c]	4.5	0	0[c]
4	$\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{Bn}$	12.7 (17)	30.2 (36)	21.5	9.6	22
5	$\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{Oct}^t$	24.0 (31)	54.8 (65)	43	16.1	20
6	$\mathbf{7}_4 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{Oct}^t$	15.8 (15)	31.5 (37)	21.5	9.2	20
7	$\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{Bn} \cdot \mathrm{Bn}$	5.1 (7.1)	4.7 (5.6)	3.5	Trace	~0
8[d]	$\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{Bn} \cdot \mathrm{Bn}$	5.6 (7.8)	4.7 (5.6)	5.5	Trace	~0
9	$\mathbf{5}_3 \cdot \mathrm{Br}$	45.9 (71)	111.1 (130)	96	52.5	33

[a] Mixture was stirred at room temperature overnight unless otherwise noted

[b] Calculated from recovery (%) of C_{70} in filtrate

[c] C_{60}

[d] At −30 °C

Table 4 Selective precipitation of C_{70} with *p*-halohomooxacalix[3]arenes ($\mathbf{5}_3$ and $\mathbf{7}_3$) with various substituents[a]

Run	Host	Weight (mg) (μmol)	Fullerene mixture C_{60}(mg)/C_{70}(mg) (ratio)	Toluene (mL)	Precipitate		Filtrate
					C_{60}/C_{70}^{b}	Yield (%)[c]	C_{60}/C_{70}^{b}
1	$\mathbf{5}_3 \cdot \mathrm{I}$	6.9 (8.8)	2.6/13.0 (17/83)	7	8/92	93	63/37
2	$\mathbf{5}_3 \cdot \mathrm{I}$	12.8 (16)	20.3/20.4 (50/50)	11	24/76	88	86/14
3	$\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{Br}$	17.0 (23)	20.2/20.2 (50/50)	11	24/76	93	91/9
4[d]	$\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{Bn}$	11.6 (15)	10.2/9.9 (50/50)	11	14/86	18	55/45
5[d]	$\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{I} \cdot \mathrm{Oct}^t$	41.3 (53)	20.9/21.7 (49/51)	17	11/89	20	55/45
6	$\mathbf{7}_3 \cdot \mathrm{I} \cdot \mathrm{Br} \cdot \mathrm{Br}$	15.3 (22)	19.6/20.1 (50/50)	11	24/76	90	87/13
7	$\mathbf{5}_3 \cdot \mathrm{Br}$	15.3 (24)	20.1/19.8 (50/50)	11	38/62	91	84/16
8	$\mathbf{5}_3 \cdot \mathrm{Br}$	11.5 (18)	4.0/16.2 (20/80)	7	12/88	84	45/55
9	$\mathbf{5}_3 \cdot \mathrm{Br}$	8.0 (12)	10.0/9.8 (50/50)	6	23/77	75	76/24
10	$\mathbf{5}_3 \cdot \mathrm{Br}$	7.4 (11)	9.8/10.0 (50/50)	10 + 5[e]	22/78	79	78/22
11	$\mathbf{5}_3 \cdot \mathrm{Br}$	7.3 (11)	10.2/9.8 (50/50)	5 + 5[f]	21/79	76	78/22
12	$\mathbf{5}_3 \cdot \mathrm{Cl}$	11.6 (23)	9.7/9.7 (50/50)	5	48/52	93	67/33
13	$\mathbf{5}_3 \cdot \mathrm{Cl}$	12.1 (24)	20.2/20.1 (50/50)	11	37/63	63	63/37
14	$\mathbf{5}_3 \cdot \mathrm{F}$	10.9 (24)	9.8/9.8 (50/50)	5	6/94	19	55/45

[a] Mixture was stirred at room temperature overnight unless otherwise noted

[b] Weight ratio based on area ratio on HPLC

[c] Yield of C_{70} in precipitate was calculated from weights of C_{60} and C_{70}, and C_{60}/C_{70} ratios of precipitate and filtrate

[d] At −30 °C for 2 days

[e] Toluene (10 mL) + hexane (5 mL)

[f] 1,1,2,2-Tetrachloroethane (5 mL) + hexane (5 mL)

Table 4 [12]. The selectivity and the yield of C_{70} strongly depend on the kind of halogens at the *para* position in the host molecules. The order of efficiency in the purification of C_{70} followed the size of the halogens, I > Br > Cl > F (runs 2, 7, 13 and 14). As compared to $\mathbf{5}_3 \cdot \mathrm{I}$ and $\mathbf{5}_3 \cdot \mathrm{Br}$, $\mathbf{5}_3 \cdot \mathrm{Cl}$ gave low selectivity (run 12) or low yield of C_{70} (run 13), and $\mathbf{5}_3 \cdot \mathrm{F}$ afforded low yield of C_{70} with the highest purity (run 14). When $\mathbf{5}_3 \cdot \mathrm{I}$ or $\mathbf{5}_3 \cdot \mathrm{Br}$ was added to a toluene solution of a fullerene mixture ($C_{60}/C_{70} = 1/1$, w/w), the ratios of C_{60}/C_{70} and the yields of C_{70} of the precipitates ranged 21/79–38/62 and 75–91%, respectively (runs 2, 7 and 9–11). The purity of C_{70} in the precipitates increased to 92% and 88% from 83% to 80%, respectively, after the selective precipitation (runs 1 and 8). The attempt to obtain pure C_{70} by this method was not successful; 92% purity was the upper limit of this purification. *p*-Iodohomooxacalix[3]arenes with one or two Br groups, $\mathbf{7}_3 \cdot I \cdot I \cdot Br$ and $\mathbf{7}_3 \cdot I \cdot Br \cdot Br$ (runs 3 and 6), afforded almost the same results as that of $\mathbf{5}_3 \cdot I$ (run 2), while the ones with one alkyl group, $\mathbf{7}_3 \cdot I \cdot I \cdot Bn$ and $\mathbf{7}_3 \cdot I \cdot I \cdot Oct^t$, gave much lower yields of C_{70} (runs 4 and 5). These results show that three heavy halogens are essential for the hosts to obtain both good yield and selectivity. The selectivity seems to be similar to the reported ones with *p*-*tert*-butylcalix[6]arene [87, 91]. When other solvent systems were used instead of toluene, similar results were obtained as shown in runs 10 and 11.

The precipitate formed from a toluene solution of fullerene mixture ($C_{60}/C_{70}/C_{>70} = 2/6/2$) with $\mathbf{5}_3 \cdot I$ included a considerable amount of higher fullerenes ($C_{>70}$) along with C_{70}, indicating that $\mathbf{5}_3 \cdot I$ can not discriminate C_{70} and $C_{>70}$ [12]. This is another limitation of this method for applying to a practical purification of fullerenes. When a toluene solution of $\mathbf{5}_3 \cdot I$ was added to a toluene solution of raw fullerene mixture (fullerene extract, $C_{60}/C_{70} = 8/2$), precipitation was not observed to give a dark brown homogeneous solution. In order to recover the fullerene and reuse the host molecules, liberation of the complexes was carried out. Since the binding of the C_{70} complexes with $\mathbf{5}_3 \cdot I$, $\mathbf{7}_3 \cdot I \cdot I \cdot Br$ and $\mathbf{7}_3 \cdot I \cdot Br \cdot Br$ was very tight, it was very difficult to liberate by a simple way as that employed for the *p*-*tert*-butylcalix[8]arene-C_{60} complex [90, 91]. Eventually, C_{70}-$\mathbf{5}_3 \cdot I$ was dissolved in *o*-dichlorobenzene, and the host molecules were extracted with basic aqueous solution.

Highly practical method for fullerene purification by filtration through activated carbon layer

In 2003, when we published the results of the fullerene purification using host-guest strategy mentioned above [12], commercial production of fullerene mixture was started by consecutive combustion process [133, 134] developed by Frontier Carbon Co. [135]. Although the technological innovation lowered the price of fullerene mixture remarkably to less than 1/4 compared to the former price, pure C_{60} and C_{70} were still expensive because of their post-synthesis using chromatographic separation of fullerene mixture [79, 136–141].

For separation of fullerenes [79, 136], sublimation was used at the first macroscopic synthesis of C_{60} [2]. Since the fullerene extract has to be repeatedly sublimed at the sacrifice of the yield to obtain pure sample, the method is concluded to be ineffective for the isolation of a fullerene from the mixture (fullerene extract) [79]. As soon as fullerene was known to be solubilized into some organic solvents [2], chromatographic separation using alumina and hexanes as stationary and mobile phases, respectively, was reported by Taylor et al. [142] and Whetten et al. [143] in 1990. Because of the low solubility of hexane and low retention of alumina to fullerenes, the chromatographic separation was tedious and time-consuming [144, 145]. Therefore, the stationary phase showing appropriate retention of fullerenes has been explored to improve the chromatographic techniques to industrial scale purification of fullerenes. In 1992, carbon materials such as coal and graphite was found to be employed as a stationary phase showing strong retention of fullerenes [141, 146]. In order to reduce the absorption by the carbonaceous stationary phase, silica gel was mixed with AC to realize gram-scale purification of C_{60} [140]. Since then, a mixed system of AC with silica gel or alumina has been used mainly as a stationary phase in the chromatographic separation of fullerenes [137–139, 147–149].

Although chromatographic methods are quite useful for laboratory-scale purification, they possess fundamental drawbacks on the application to the larger-scale production such as limited column loadings, duration of the process with constant attention, and the amounts of both stationary and mobile phases required. Non-chromatographic methods such as selective complexation [11, 12, 90, 91, 150] and fractional crystallization [151–154] are not always efficient especially for large-scale purification, because they require stirring for a long time sometimes at elevated temperature and repeating precipitation-filtration sequence a few times. Therefore, there was a great demand for more efficient purification method exploitable for large-scale production of pure fullerenes. Such situation of fullerene production led the author to explore practical purification method of fullerenes. Eventually, we developed a very fast, facile and inexpensive method for the purification of C_{60} and C_{70} by passing a solution of fullerene extract through thin layer of AC, which is promising for industrial-scale production [13, 14, 32]. Since another method of large-scale purification of C_{60} was reported recently by Nagata et al. (Frontier Carbon Co.) using selective precipitation of $C_{\geq 70}$ with DBU [155], the efficiency of our filtration method will be compared with that of the selective precipitation methods using DBU and calix[8]arene in the last part of this section.

The key for developing this practical process is the finding of highly efficient AC as an adsorbent by examining many kinds of powdered, fibrous and granular ACs. When powdered W-15, which is fibrous AC manufactured by Unitica Ad'all, was employed as a filter bed, we observed too strong retention of C_{60} by use of toluene as an eluent but an appropriate retention when using chlorobenzene [32]. In order to understand the difference in the efficiency of the ACs, we compared the analytical results

Table 5 Purification of C_{60} with various solvents in filtration method[a]

Run	Solvent	Activated carbon (g)[b]	Thickness of carbon layer (mm)	Retention of C_{60} (mL)[c]	C_{60} filtrate (mL)[d]	Yield of C_{60} (%)[e]
1	TMB	10.8	17	98	167	91
2	PhCl	9.0	15	144	285	84
3	*o*-xylene	10.8	16	160	206	82
4	*o*-$Cl_2C_6H_4$	12.6	18	55	43	61

[a] Solution of fullerene mixture (1.80 g) was filtered

[b] Activated carbon fiber (W-15) powdered by high-shear mixer was layered on Kiriyama funnel™ of 40 mm diameter. The amounts were optimized except for run 4 where larger amount of adsorbent should be needed to increase yield

[c] The amount of filtrate when C_{60} started to elute

[d] Volume of filtrate including pure C_{60}

[e] Based on the quantity of C_{60} in the starting fullerene mixture

of their pore size distributions, X-ray diffraction and elemental composition. This revealed that W-15 has larger pore volume in the range of 1.0–2.0 nm, which is slightly larger than the diameter of fullerenes, larger degree of graphitization and less oxygen content than the other fibrous ACs manufactured by Unitica Ad'all: W-10, A-20 and A-15 [32]. Since the retention of fullerenes is ascribed to π–π interaction between the fullerene surface and fused polyaromatics in the pores of AC, W-15 is considered to have a great advantage for the appropriate retention. That is, W-15 has a larger number of pores appropriate for the capture and release of fullerenes, more developed graphitic area capable of interacting with fullerenes and a smaller fraction of polar functional groups responsible for hydrophobic character [32].

After thorough investigation of the filtration conditions, we found that various solvents with higher fullerene solubility could be applied to this process [14]. The results are summarized in Table 5. Although *o*-dichlorobenzene, one of the most frequently used solvents with very high fullerene solubility, reduced the volume of the solvent remarkably (run 4), the yield of pure C_{60} was not high enough (61% yield) because of the low resolution between C_{60} and C_{70}. Therefore, we examined the solvents with solubility between chlorobenzene and dichlorobenzenes, and found that TMB gave the highest yield of pure C_{60} (91% in run 1) among the four solvents examined. In addition, smaller volume of solvent was required in TMB than chlorobenzene and *o*-xylene.

The optimum conditions were employed for the large-scale purification of C_{60} and C_{70} as shown in Table 6 [14]. Purification of 0.45 g of fullerene mixture provided 91 % and 23% yields of C_{60} and C_{70}, respectively (run 1). When 1.8 g of fullerene mixture was purified, the yields of C_{70} increased to 28% and 29% in runs 2 and 3, respectively. However, the use of smaller amount of AC (9.0 g, AC/fullerene mixture (w/w) = 5) lowered the yield of C_{60} to 83% (run 3), indicating that the best ratio of AC/fullerene

Table 6 Purification of C_{60} and C_{70} in large scale by filtration method[a]

Run	Fullerene mixture (g)	Activated carbon[a] (g)	Thickness of carbon layer (mm)	Diameter of funnel[b] (mm)	Retention of C_{60} (mL)[c]	C_{60} filtrate (mL)[d]	Third filtrate (mL)[e]	C_{70} filtrate (mL)[f]	Yield of C_{60} (%)[g]	Yield of C_{70} (%)[h]
1	0.45	2.7	13	21	24	45	70	120	91	23
2	1.8	10.8	18	40	111	201	200	450	92	28
3	1.8	9.0	15	40	82	109	200	400	83	29
4	9.1	54.6	15	95	400	524	1000	2000	82	28

[a] W-15 was powdered by shearing with a mixer and/or by grinding in a mortal with a pestle

[b] Kiriyama funnel™

[c] The amount of filtrate when C_{60} started to elute

[d] The filtrate included C_{60} in >99% purity

[e] The filtrate included mixture of C_{60} and C_{70}

[f] The filtrate included C_{70} in 93–94% purity

[g] Based the quantities of C_{60} in the starting fullerene mixture. Purity of C_{60} is more than 99%

[h] Based the quantities of C_{70} in the starting fullerene mixture. Purity of C_{70} is 93–94%

mixture (w/w) is 6 rather than 5. In the largest scale purification using 9.1 g of a fullerene mixture with a 95 mm Kiriyama funnel, total ~4 L of TMB was passed through the AC layer with only 15 mm thickness over 40 min to give 4.60 g (82 % yield) of pure C_{60} and 0.63 g (28 % yield) of C_{70} of 93% purity. For obtaining pure C_{60} only, however, less than 1 L of TMB eluted over 10 min was enough by use of the powdered AC fiber (54.6 g) in this process (run 4), while 7 L of toluene eluted over 25 min was required in the purification of the same amount of the fullerene mixture filtered through a layer of 80.0 g of the AC powder [32].

The filtration process described so far possesses the following characteristics as compared to the process of selective precipitation with DBU [155] and calix[8]arene [90, 91]. Firstly, TMB extract of fullerene mixture was directly submitted to this process without any pretreatment. No post treatments other than concentration were required after filtration. In contrast, the purification method by selective complexation with DBU and calix[8]arene required post treatment of filtration and washing [90, 91, 155]. Secondly, C_{70} can be purified in this filtration-based process in contrast to the selective complexation, though the efficiency should be improved to obtain a large amount of pure C_{70}. Lastly, TMB recovered after concentration can be recycled without any treatment. In the selective precipitation with DBU mentioned above, on the other hand, recycle of TMB is not so easy as our method because methanol was added to the C_{60} solution in TMB for the precipitation of pure C_{60}.

Selective complexation of porphyrins with fullerenes

Most of the host molecules for fullerenes have been designed based on the idea of match in shape. According to the concept, the above-mentioned host molecules with concave shapes such as calixarenes [11, 12, 71, 73, 75–78, 80], cyclodextrins [74, 76, 78, 80, 86, 94, 95–108], cyclotriveratrylenes [76, 109–111] and carbon nanorings [113–118] were designed and shown to exhibit large binding constants for fullerenes as expected. However, it was recognized that concave–convex host-guest combination is not always necessary to realize strong supramolecular interaction of fullerenes. Although porphyrins are almost flat molecules, tetraphenylporphyrin-linked silica stationary phase was found to be effective for chromatographic separation of fullerenes with curved π-surface in 1993 [156–159]. A close contact (less than 3.0 Å) between porphyrin plane and curved fullerene surface was observed in the crystal structures of the complex of C_{60}-octakis(dimethylamino)porphyrazine in 1995 [160] and covalently linked fullerene-porphyrin conjugate in 1997 [161]. The strong interaction was also confirmed by many cocrystallites of octaethylporphyrins [162, 163], tetraphenylporphyrin and its derivatives [164–167], metal tetrakis(4-pyridyl)porphyrins [168, 169], and dendritic porphyrins [125, 170] with C_{60}, $C_{60}O$, C_{70} $C_{120}O$, methanofullerene and endohedral metallofullerenes (M@C_{80}) [72, 119, 122]. Host molecules consisting of two or more porphyrin units were also developed, such as cyclic diporphyrins [121, 126, 127, 171–175], gable-type diporphyrins [120, 176–181], porphyrin tetramer [124], and porphyrin hexamer [123]. They exhibited very large binding constants and, in some cases, good C_{60}/C_{70} selectivities [119].

Although there exists a number of examples of porphyrin-based hosts for fullerenes as mentioned above, we investigated complexation behavior of porphyrin monomers (**9**–**11**) [15, 182] and dimers (**12** and **13**) [15, 19, 20, 183] shown in Fig. 2 for fullerenes in solution [15, 16, 17, 18]. In particular, the complexation of fullerenes with the dimers (**12** and **13**) was a model for the CNT extraction, which will be mentioned below, and gave us valuable information to achieve it [19, 20].

The binding constants of the porphyrins for C_{60} and C_{70} (K_{C60} and K_{C70}, respectively) were determined by fluorescence and absorption spectral change upon the titration of fullerenes to the porphyrin solutions. The results are summarized in Table 7. All the porphyrins show large binding constants in the range of 10^3–10^4 M^{-1} and 10^4–10^5 M^{-1} for K_{C60} and K_{C70}, respectively. The K_{C70} is 4–11 times larger than K_{C60} with all the porphyrins except **12** · Ni [18].

The energy-minimized structures in computational calculations of the complexes reveal that C_{60} and C_{70} are encapsulated in the cleft of the diporphyrin nanotweezers as shown in Fig. 3 [18]. Side-on orientation of C_{70} is calculated to be more stable than end-on in all the cases except for **12** · Ni, indicating that the dominant interaction between them is π–π interaction. In the case of **12** · Ni-C_{70} complex [18], slightly larger energy of stabilization is given to the end-on rather than side-on interaction of C_{70}, implying that dispersive forces associated with π–π interactions may not the be dominant factor in fullerene-**12** · Ni interactions [164]. Electrostatic interaction between electron-negative 6–6 juncture of the fullerene and electron-positive center of the porphyrins is proposed as the nature of the interaction other than the π–π interaction [119, 179].

The largest binding constants ($K_{C60} = 2.9 \times 10^4$ M^{-1} and $K_{C70} = 1.4 \times 10^5$ M^{-1}) were obtained in **12** · Zn [16] which were about 10 times larger than those of the other porphyrins in both K_{C60} and K_{C70}. As compared to other tweezer-type diporphyrins with somewhat flexible spacers, **12** · Zn shows comparable or larger binding constants in complexation with both C_{60} and C_{70}; that is, K_{C60} of

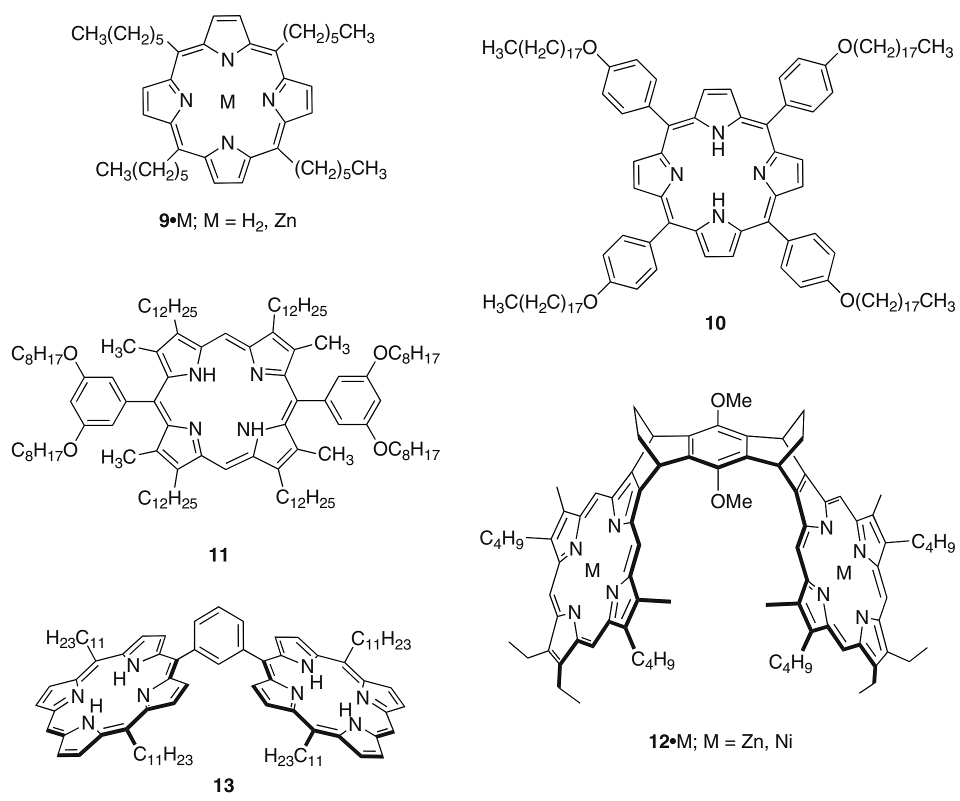


Fig. 2 Structures of porphyrin monomers and dimers investigated for the complexation behavior with C_{60} and C_{70}

Table 7 Binding constants of porphyrin monomers (**9**–**11**) and dimers (**12** and **13**) for C_{60} (K_{C60}) and C_{70} (K_{C70}), and their ratios

Porphyrin	Fluorescence			UV–Vis		
	K_{C60} (M^{-1})	K_{C70} (M^{-1})	K_{C70}/K_{C60}	K_{C60} (M^{-1})	K_{C70} (M^{-1})	K_{C70}/K_{C60}
9 · H_2	1.7×10^3	1.5×10^4	8.5	2.6×10^3	1.8×10^4	6.8
9 · Zn	2.2×10^3	2.5×10^4	11	3.4×10^3	1.4×10^4	4.1
10	1.6×10^3	1.4×10^4	8.7			
11	1.9×10^3	1.8×10^4	9.4			
12 · Zn	2.9×10^4	1.4×10^5	4.9	3.4×10^4	2.5×10^5	7.4
12 · Ni	1.7×10^4	4.0×10^4	2.4	1.6×10^4	1.9×10^4	1.2
13	2.0×10^3	1.4×10^4	7.2			

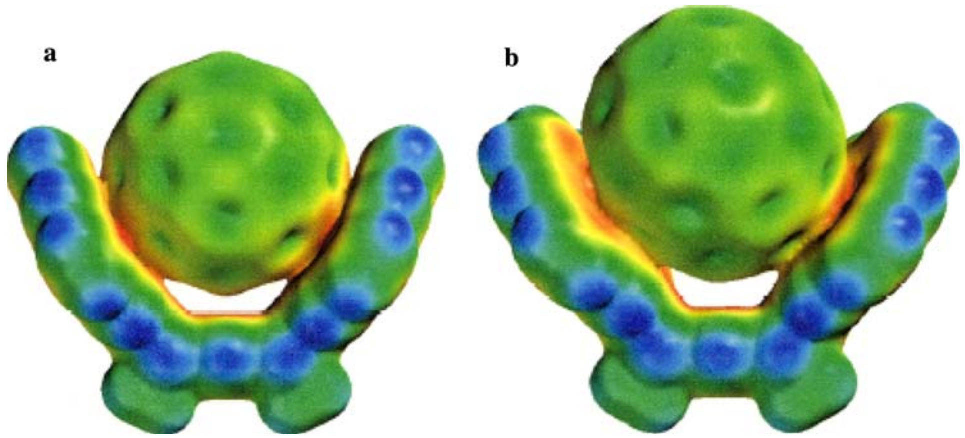


Fig. 3 Ab initio optimized geometric structures of **12** · Ni complexes with (**a**) C_{60} and (**b**) C_{70} in molecular electrostatic potential maps. Red-yellow and blue-green colors indicate negative and positive electron potential, respectively

12 · Zn is similar to that of Pd diporphyrin cleft ($3.7 \times 10^4\ \mathrm{M}^{-1}$) [177] and about 3–10 times larger than those of calixarene diporphyrins ($8.6 \times 10^3\ \mathrm{M}^{-1}$) [180], thiacalixarene diporphyrin ($2.7 \times 10^3\ \mathrm{M}^{-1}$) [180] and Jaws diporphyrin ($5.2 \times 10^3\ \mathrm{M}^{-1}$) [178, 179]. For the complexation with C_{70}, **12** · Zn also shows about 4–30 times larger binding constant than those of calixarene diporphyrin ($2.8 \times 10^4\ \mathrm{M}^{-1}$) and thiacalixarene diporphyrin ($3.7 \times 10^4\ \mathrm{M}^{-1}$ [180] and $5.0 \times 10^3\ \mathrm{M}^{-1}$ [181]). However, cyclic porphyrin dimers [121, 126, 127, 171–175], preorganized porphyrin dimer [120], and porphyrin tetramer [124] and hexamer [123] show higher binding affinity towards C_{60} ($K = 10^5$–$10^8\ \mathrm{M}^{-1}$).

Another interesting aspect in the host-guest chemistry of fullerenes and porphyrins is preference of C_{70} over C_{60} (K_{C70}/K_{C60} shown in Table 7). The average selectivities of K_{C70}/K_{C60} in porphyrin monomers (**9–11**) and dimers (**12** and **13**) are 8.0 and 4.6, respectively. Interestingly, porphyrin monomer exhibits higher C_{70} selectivity than dimer. The average selectivity of the porphyrin monomer ($K_{C70}/K_{C60} = 8.0$) is larger than those of azacalix[*m*]arene [*n*]pyridine (~1.9) [184] and calixarene diporphyrin (~4.3) [180]. However, the selectivity is lower than those observed in carbon nanoring (~16) [32], cyclic dimers of Zn-porphyrins (~25) [127] and H_2-diporphyrin (~32) [126], and tweezer-type biscyclotriveratrylene (~14) [111].

It is noteworthy to add that azulenes, which are flat hydrocarbon molecules consisting of fused five and seven membered rings, have been found quite recently to show large binding constants (10^4–10^5) [185]. The binding constants (K_{C60} and K_{C70}) of azulenes are comparable to or even larger than those of **12** · Zn, and much larger than that of the structural isomer, naphthalene [186, 187]. Unlike the case of porphyrins shown in Table 7, azulenes do not discriminate C_{60} and C_{70}, implying that π–π interaction may not be the dominant attractive force in azulene-fullerene complexes like **12** · Ni-fullerene complexes mentioned above [164].

Optical resolution of single-walled carbon nanotubes by chiral diporphyrin nanotweezers

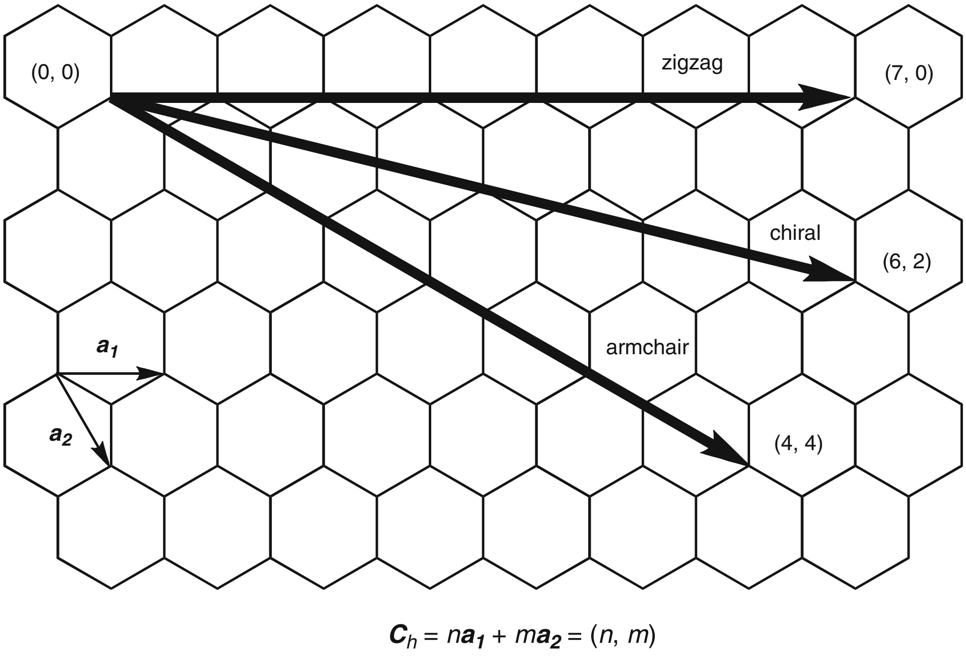
Structures and terminology of carbon nanotubes

The structures of CNTs are defined by a variety of parameters such as a number of carbon layers, length, diameter and an alignment of hexagons. Broadly, CNTs are classified into the following three types according to the number of carbon layers; SWNTs, DWNTs and MWNTs. All these three types of CNTs were selectively synthesized by use of different combination of metal catalysts under different conditions [188–194].

Among the three types of CNTs, SWNTs attract growing interest because of their simple structures and electronic properties [195, 196]. The structure of a SWNT can be prepared by rolling up a graphene sheet into a seamless cylinder. 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 roll-up index (*n*, *m*) as shown in Fig. 4 [197, 198]. The following three types of SWNTs can be formed; zigzag, armchair and chiral as shown in Fig. 5, depending on the alignment of the hexagonal rings along the tube axis. The (*n*, *m*) and $\boldsymbol{C}_h$ have been referred to as "chiral" index (or simply "chirality") and "chiral" vector, respectively, in the CNT society. However, the meaning of the "chiral" is not always consistent with the original meaning of chiral in chemistry; that is, "the geometric property of a rigid object of being non-superposable on its mirror image" [199]. While chiral SWNTs have non-superposable mirror-image structures, left- and right-handed ones shown in Fig. 6, zigzag and armchair structures do not have their non-superposable mirror-image. 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 the CNT society. As Strano pointed out in his article [200], this terminology is very confusing and, hence, a systematic nomenclature is required to define the structures of CNTs. The terms "roll-up" index and "roll-up" vector are proposed to be used instead of "chiral" index and "chiral" vector, respectively, to indicate (*n*, *m*) [19, 20]. In this review, the term chiral is used exclusively in the meaning of having the non-superposable property on its mirror image. The "roll-up" index (or simply index) indicates the (*n*, *m*) of a CNT and does not include any information about stereochemistry (chirality), which will be discussed below.

Quite recently, optically active SWNTs have been obtained through the optical resolution of their left- and right-handed helical structures by our group [19]. For the expression of the stereoisomers of chiral SWNTs, however, a variety of terms have been used so far; *LH* and *RH* [19], *r* and *l* [201], *L* and *R* [202], (n_1, n_2) and (n_2, n_1) [203], and *AL* and *AR* [197]. Since stereochemistry of SWNT will be discussed much more than before optically active SWNTs were obtained, definite nomenclature is required for the stereochemistry of SWNTs [200]. In the recent paper from our group [19, 20], left- and right-handed helical structures on the basis of the definition of *AL* and *AR* [197] are referred to as *M* and *P*, respectively, according to the IUPAC terminology [199]. Every SWNT has three armchair lines (A lines) as indicated as solid arrows in Fig. 7. These A lines cannot be superposed on its mirror-image in the case of chiral SWNTs, while the corresponding A lines can be superposed in zigzag and

Fig. 4 (n, m) SWNT defined by rolling up the graphene along the roll-up vector $\boldsymbol{C}_h$



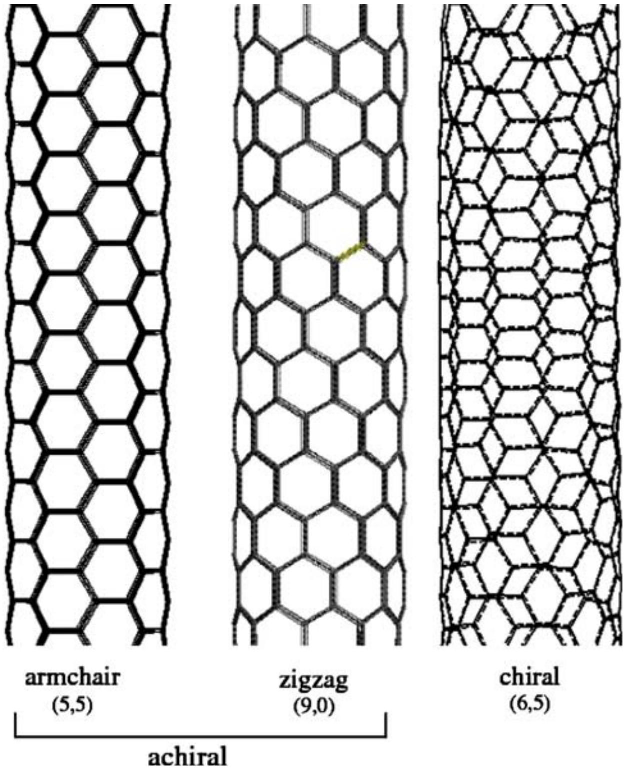


Fig. 5 Armchair, zigzag, chiral structures of SWNTs

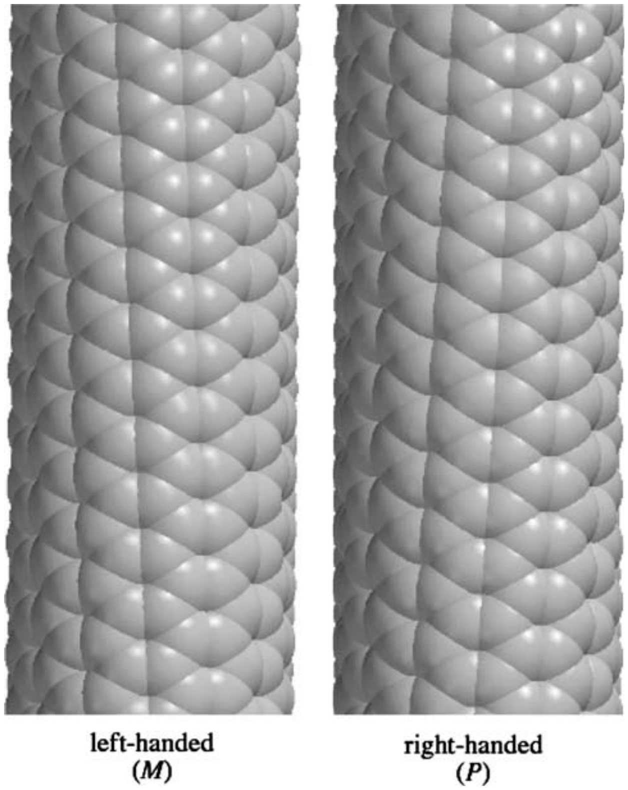


Fig. 6 Chiral (6,5) SWNTs with left- and right-handed structures corresponding to *M* and *P* helical structures according to the IUPAC nomenclature

armchair types. When the two out of the three A lines are directed toward the left side of the SWNT axis and the third A line toward the right, the chiral SWNT is designated as *M* as shown in Fig. 7a. On the other hand, the chiral SWNT with two A lines being directed toward the right of the SWNT axis is *P* as shown in Fig. 7b. This review follows this terminology.

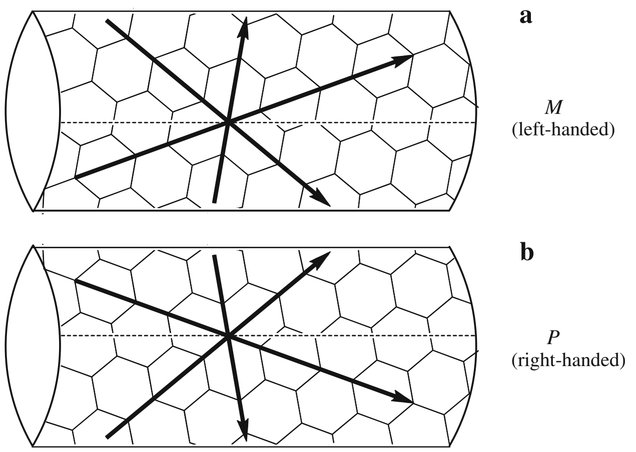


Fig. 7 Definition of *M* (left-handed) and *P* (right-handed) of SWNTs. Three arrows and dashed line indicate armchair lines (A lines) and SWNT axis, respectively

Optically active single-walled carbon nanotubes through extraction with chiral diporphyrin nanotweezers

It is well-known that the physical properties of SWNTs are closely correlated to their structures. SWNTs with controlled structures are, therefore, in great demand both for fundamental studies and technological applications [23]. So far, however, the range of their electric and optical applications has remained rather limited, because as-prepared SWNTs comprise different structures which vary in length, diameter and roll-up index. Extensive investigations have been made in pursuit of selective synthesis and separation of SWNTs with specific structural properties. As for the synthesis, limited roll-up indices of SWNTs have been selectively prepared, using a silica-supported Co-Mo catalyst [193, 194] and the catalyst system of Co-incorporated mobile composition of matter 41 (Co-MCM-41) [204, 205]. Enrichment and separation of metallic and semiconducting SWNTs have been achieved by drawing on the differences in their electric or electronic properties [206–214]. Separation based on length, diameter and/or roll-up index of SWNTs have been conducted by using chromatography [215–220] and polymer-assisted extraction [221, 222]. Little attention, however, has been paid to another important feature concerning the structures of carbon nanotubes, namely the optical isomers that arise from the spiral alignment (either left- or right-handed) of the hexagonal carbon rings along the nanotube axis in chiral SWNTs.

SWNTs other than the armchair and zigzag types shown in Fig. 5 are intrinsically chiral, and their helical structures have been atomically observed by scanning probe microscopy [223, 224] and transmission electron microscopy [202, 225, 226]. Although their optical properties have been predicted theoretically [197, 198, 227, 228], optical activity originating solely from carbon nanotubes has not been reported so far. Quite recently, SWNTs wrapped with DNA were reported to be CD-active, but become CD-inactive upon the replacement of DNA with SDBS, an achiral surfactant [229]. We have found optically active SWNTs for the first time by preferentially extracting either (*M*)- or (*P*)-stereoisomers with chiral porphyrin dimers [19, 20].

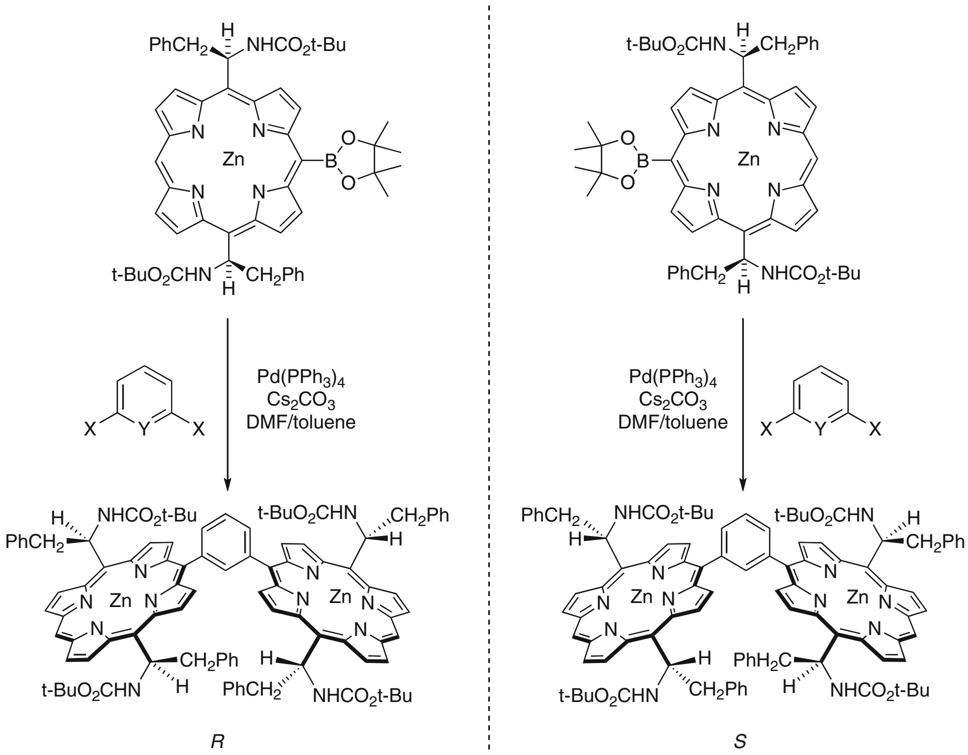
Chiral diporphyrin nanotweezers **14** and **15** were prepared via Suzuki-Miyaura coupling reactions of the corresponding boronated (*R*)- or (*S*)-monoporphyrin with 2,6-dibromopyridine and 1,3-diiodobenzene, respectively, as shown in Scheme 9 [19, 20]. SWNTs (CoMoCAT, SouthWest NanoTechnologies, Inc.) [193] were extracted in methanol with the chiral diporphyrins. After concentration of the extract, the chiral diporphyrins were removed by washing with pyridine, and the SWNTs were dissolved into D_2O with the aid of SDBS [230]. The resulting solutions were analyzed with CD as shown in Figs. 8 and 9.

The solutions of SWNTs extracted by (*R*)- and (*S*)-diporphyrins show symmetrical CD spectra as shown in Fig. 8 [19, 20]. While the CD intensities are not so different among the peaks corresponding to the roll-up indices of SWNTs extracted with **15**, SWNTs extracted by **14** show two prominent CD peaks at 562 and 341 nm corresponding to E_{22} and E_{33} (the second and third optical transition energy) of the (6,5)-SWNTs, respectively [231]. These spectral features suggest much higher discrimination ability of **14** to the helical structures of (6,5)-SWNTs. The CD signs corresponding to (6,5)-SWNTs are observed to be alternate at 341, 562 and 980 nm (Fig. 9); that is, (+, −, +) for (6,5)-SWNTs extracted with (*S*)-**14** and (−, +, −) for those extracted with (*R*)-**14**. These alternate features are consistent with the theoretical prediction [197, 198, 227, 228], hence indicating optical activities of the extracted SWNTs [19, 20]. The similar alternate spectral features are also observed for (8,4)-SWNTs at 603 and 386 nm that are assigned to E_{22} and E_{33} transitions (Fig. 9).

Extraction abilities of **14** and **15** were quantified by measuring the amounts of porphyrin-free SWNTs in the extraction experiments [19, 20]. Tweezers **14** extracted ~50% of SWNTs, whereas tweezers **15** extracted less than 5% of SWNTs. This enhanced extraction ability of **14** 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 index. The choice of an appropriate spacer unit is found to be one of the most important factors for separating SWNTs in this host-guest strategy.

Scheme 9 Synthesis of chiral diporphyrin **14** and **15** through Suzuki-Miyaura coupling reaction



14: X = Br, Y = N
15: X = I, Y = CH

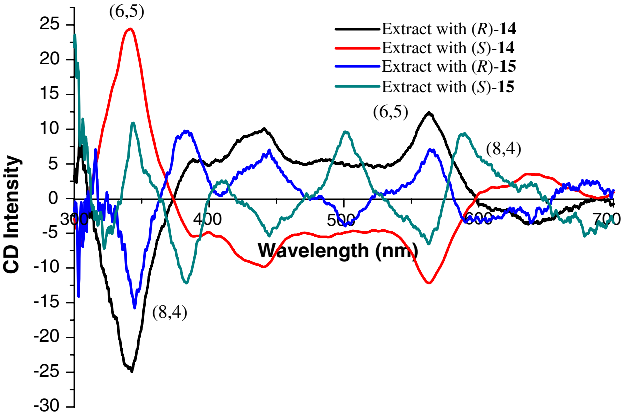


Fig. 8 CD spectra of the D_2O/SDBS solutions of SWNTs extracted with (*R*)-**14**, (*S*)-**14**, (*R*)-**15** and (*S*)-**15**. The concentration of SWNTs in these solutions was normalized by their absorption peaks at 980 nm

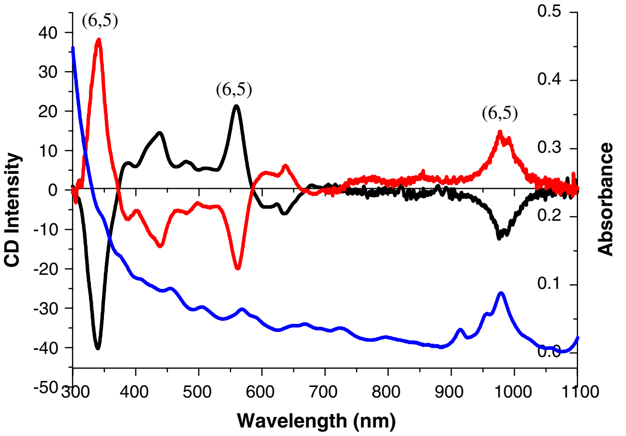


Fig. 9 CD spectra of the D_2O/SDBS solutions of SWNTs extracted with (*R*)-**14** (*black line*) and (*S*)-**14** (*red line*), and UV-VIS spectra of the D_2O/SDBS solution of SWNTs extracted with (*R*)-**14** (*blue line*). The concentration of SWNTs in these solutions was normalized by their absorption peaks at 980 nm

Computer-generated energy-minimized structures of the complexes

In order to obtain theoretical support for interpretation of the above experimental results, we carried out molecular modeling (molecular mechanics) for the complexes of (*P*)- and (*M*)-(6,5)-SWNTs (simply designated as *P* and *M*, respectively) with (*R*)- and (*S*)-**14**. The structures are shown in Figs. 10a and b [19, 20].

In Fig. 10a, two sets of enantiomers, *P*:(*R*)-**14** and *M*:(*S*)-**14**, and *P*:(*S*)-**14** and *M*:(*R*)-**14**, show highly symmetrical mirror-images, and two sets of diastereomers, *P*:(*S*)-**14** and *M*:(*S*)-**14**, and *P*:(*R*)-**14** and *M*:(*R*)-**14**, 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 on the absorption spectra [19, 20]. The association

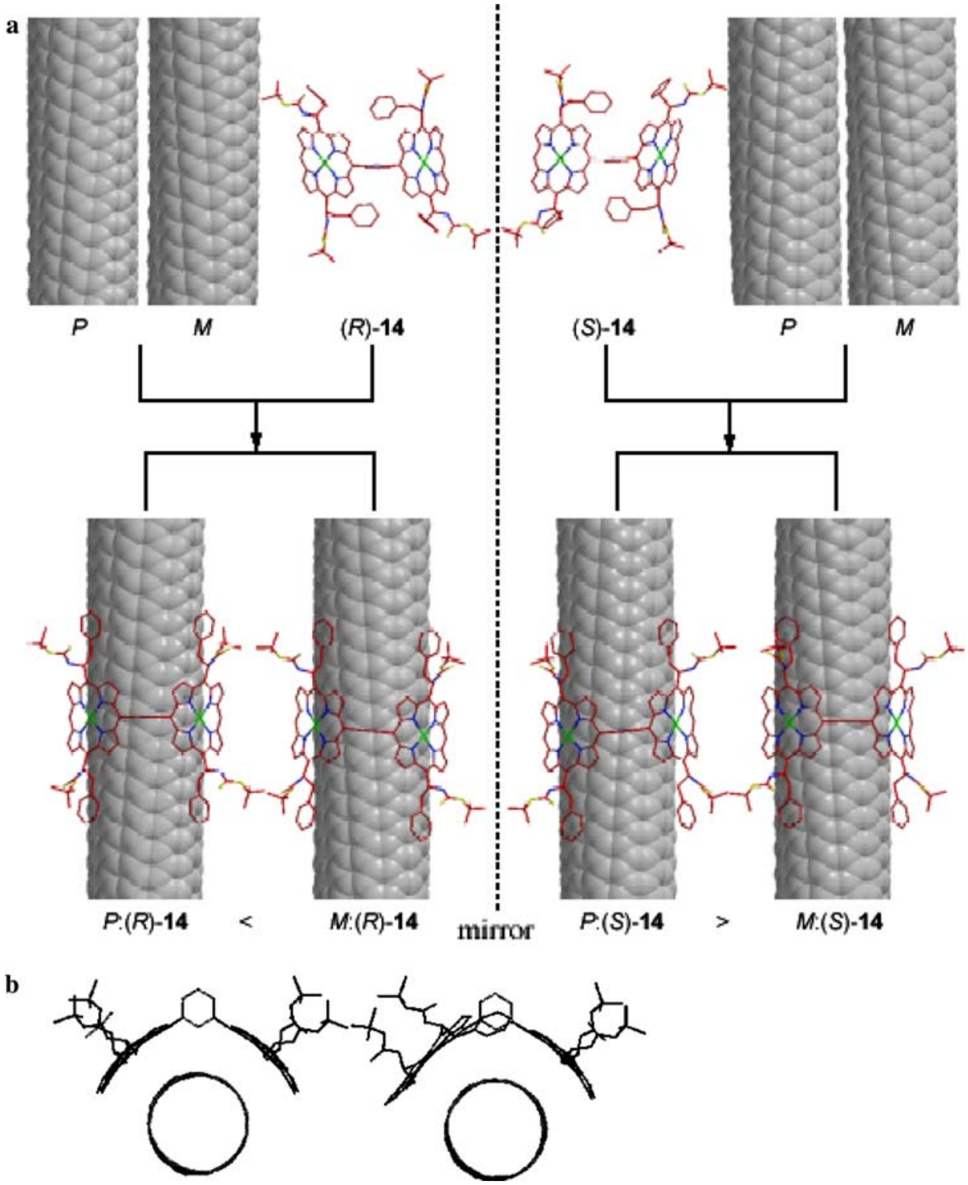


Fig. 10 Computer-generated molecular modeling of the complex structures; (**a**) side views of 1:1 complexes of (*R*)- and (*S*)-**14** with (*P*)- and (*M*)-(6,5)-SWNTs, (**b**) views of 1 : 1 complexes of (*M*)-(6,5)-SWNTs with (*R*)-**14** (left) and (*R*)-**15** (right) along the SWNT axis

enthalpies in *P*:(*R*)-**14**, *M*:(*R*)-**14**, *P*:(*S*)-**14** and *M*:(*S*)-**14** are calculated to be −57.78, −58.00, −58.00 and −57.78 kcal mol^{-1}, respectively. The difference in the energy between the diastereomers suggests that *M* and *P* are enriched by use of (*R*)-**14** and (*S*)-**14**, respectively. The same preference to the handedness of (6,5)-SWNTs was predicted in the case of **15** [19, 20].

In the complex structures depicted in Fig. 10b, the 2,6-pyridylene-bridged nanotweezers **14** fit very nicely along the curvature of the SWNT at a distance of 0.37 nm with the two porphyrin moieties bended. 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. In the complex of **15**, however, the shape compatibility of the porphyrin plane with the SWNT curvature is a little less than that of **14** and only three phenyl groups out of four locate close to the SWNT surface, making the *M*:(*R*)-**15** less stable than the *M*:(*R*)-**14**. This structural difference between these complexes is quantitatively consistent with the calculated stabilization energies: the association enthalpies for *M*:(*R*)-**14** and *M*:(*R*)-**15** are −58.00 and −56.36 kcal mol^{-1}, respectively.

The stability difference in the complex structures discussed so far should make the extraction and discrimination behavior of the 2,6-pyridylene- and 1,3-phenylene-bridged nanotweezers different.

Concluding remarks

This review has described the author's work during the last 10 years. His central field of research has been supramolecular chemistry, but his research interest has moved from synthetic organic chemistry to materials chemistry for these ten years. At present, we are working with the following three nanocarbons; fullerenes, CNTs and nanodiamonds, and focusing our effort mainly on the structural separation of CNTs and medicinal application of nanodiamonds [232–235].

As for CNTs, they have been used as mixture of various structures, which is in marked contrast in fullerenes. Therefore, SWNTs containing only limited structures are of great demand as mentioned above. Since SWNTs were first prepared [9, 10], much effort has been directed toward selective synthesis and separation of SWNTs with limited structures or specific properties [193, 206–220, 236]. Our strategy for separating SWNTs is based on the supramolecular chemistry, an advantage of which lies in the flexibility in molecular design of the host molecules. Our goal is to obtain carbon nanotubes with single structure, namely, single roll-up index with single helicity, in bulk quantity. We believe that we can make it in near future by fully utilizing our knowledge and experience in the fields of synthetic organic, supramolecular and materials chemistry.

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