Ball-, Bowl-, and Belt-Shaped Conjugated Systems and Their Complexing Abilities: Exploration of the Concave−Convex π−π Interaction

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Contents

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Hiroyuki Kurata was born in Osaka, Japan, in 1964. He received his B.S. (1988) in Chemistry from Osaka University and his Ph.D. in Organic Chemistry from Osaka University in 1993 under the supervision of Professor Masaji Oda. He became a research associate in 1994 at the Department of Chemistry, Faculty of Science, Osaka University. From 1999 to 2000, he worked at the University of Göttingen as a visiting research fellow (with Professor Armin de Meijere). His current research interests are directed toward synthesis of novel extended π systems having unique properties, especially nonplanar extended quinones and cage-shaped molecules.

1. Introduction

Since the discovery of buckminsterfullerene C_{60} (Chart 1) by Kroto, Smalley, and Curl,[1−4] a number of reports concerning new carbon allotropes having a variety of three-dimensional structures (bucky onions,[5−8] carbon nanotubes,[9,10] fullerene-peapod[10−12]) have been published. In particular, carbon nanotubes have a bright prospect of being developed into many applications to nanotechnology and nanoscience. These materials are composed of layered carbon networks having a curled and closed structure. In fact, the carbon nanotube first observed by Iijima has a multiwalled structure.[9] The concave−convex interaction (Chart 2) between the curved graphene sheets should be important for

the formation and properties of these materials. However, the nature has been little understood so far because they are hardly soluble and structurally inhomogeneous materials.
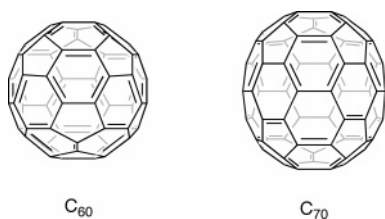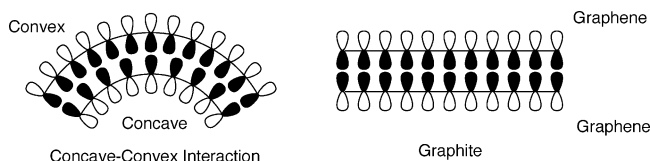
Chart 1

C_{60} C_{70}

Chart 2

Convex

Concave

Concave-Convex Interaction

Graphene

Graphene

Graphite

Figure 1. Absorption spectra of C_{60} (4.9×10^{-4} M) and C_{70} (4.9×10^{-5} M) as a function of N,N-dimethylaniline (DMA) concentration in toluene. Reprinted with permission from ref 33. Copyright 1994 American Chemical Society.

The concave−convex $\pi-\pi$ interaction should be different from the interaction between flat graphene sheets, because curved π systems such as fullerenes would be polarized in regard to the convex and concave sides, owing to the unsymmetrical nature of their p orbitals.[13−15] Contrary to the prediction, the interlayer interaction of multiwalled carbon nanotubes has been interpreted as the van der Waals (dispersion) force alone.[16,17] To understand the interaction, suitable model compounds would be needed. In this context, fullerenes, bowl-shaped conjugated systems such as corannulenes, and belt-shaped molecules have been studied both theoretically and experimentally; however, the question remains to be answered clearly. Recently, we designed and synthesized cyclic [n]paraphenyleneacetylenes ([n]CPPAs). These compounds have a smooth belt-shaped structure similar to a cut piece of carbon nanotube, and thus, they may be termed "carbon nanorings". The carbon nanorings having an appropriately sized cavity form stable inclusion complexes with fullerenes in solution as well as in the solid state (Scheme 1). The high affinity suggests that considerably strong attractive interactions would be operative between the convex and concave surfaces of the curved conjugated systems. This review surveys the supramolecular properties of the curved conjugated systems possessing a ball-shaped, bowl-shaped, or belt-shaped structure to explore the nature of the concave−convex $\pi-\pi$ interaction.

2. Fullerenes as Ball-Shaped Conjugated Systems

A survey of host molecules forming complexes with fullerenes should provide insight into the supramolecular properties of convex π surfaces. A number of excellent reviews have already been published.[18−23] This section focuses on fullerene complexes based on the concave−convex $\pi-\pi$ interaction.

2.1. Complexes with Small Molecules

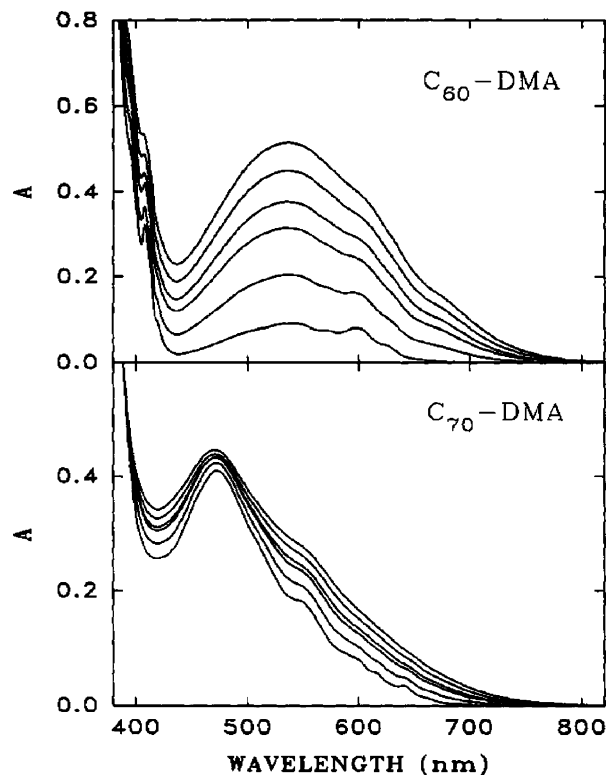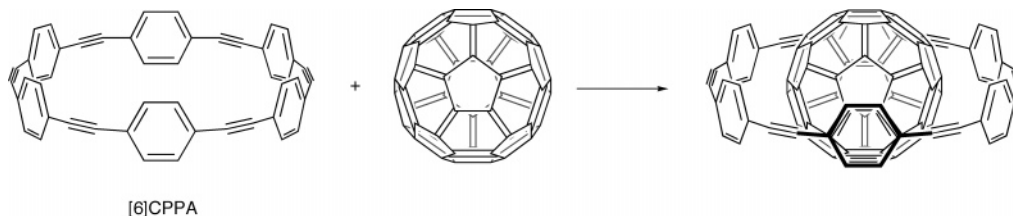Since the extraction of fullerenes from carbon soot using aromatic solvents,[24] the interaction between the curved π

surface of fullerenes and the flat π surface of aromatic compounds has been receiving much attention.[25,26] Fullerenes are tightly solvated by aromatic solvents, and they exhibit a charge-transfer (CT) absorption band in the 400−500 nm range in aromatic solvents. The CT bands show considerable solvatochromism, probably due to the formation of CT complexes between the fullerene and the aromatic solvents.[27,28] For example, CT complexes have been proposed by Wang and Rao to explain the interaction between C_{60} and aromatic amines.[29−32] Actually, the CT absorption band of C_{60} shows a drastic change with the increase of the concentration of N,N-dimethylaniline (Figure 1).[33]

The crystallographic analyses of the solvated C_{60}[34−36] and the (η^2-C_{60})Ir complex **1**[37] intuitively indicate that the face-to-face-type interaction would be operative as a dominant force in the complex formation with fullerenes (Figure 2). The molecular structure of **1** also reveals that the phenyl rings lie above a 5:6 ring fusion in the chelated C_{60}. According to the theoretical calculation, the 5:6 ring fusion represents centers of positive charge on the C_{60} surface and the 6:6 fusion represents the center of negative charge. Thus, the electrostatic interaction between electropositive 5:6 fusion and the electronegative aromatic π system has been thought to be important. A database study of the crystal structure of fullerene compounds has demonstrated that the short CH/π
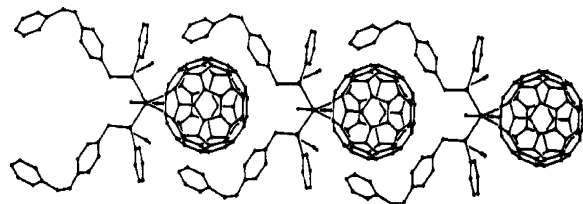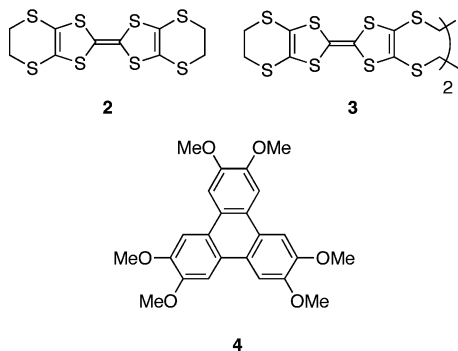
Scheme 1

[6]CPPA   +

Figure 2. Molecular packing of $(\eta^2\text{-}C_{60})$Ir (CO)Cl(bobPPh$_2$)$_2$ (**1**). Reprinted with permission from ref 37. Copyright 1992 American Chemical Society.

Chart 3

contacts frequently occur at the fullerene surface; the CH/π interaction plays a considerable part in fullerene supramolecular chemistry.[38] The database study also indicates that the hexagonal ring of C_{60} is more liable to interact with CH hydrogens, though the contrast is not significant. As the hexagonal ring of C_{60} is more electron-rich than the pentagonal one, the results are compatible with the expected electrostatic potential of the fullerene surface.

C_{60} is a weak acceptor,[39,40] and it forms superconducting complexes[41−45] by doping with alkali metals or an organic molecular ferromagnetic complex with a strong donor, such as TDAE [tetrakis(dimethylamino)ethylene].[46] These studies prompted chemists to construct CT complexes with tetrathiafulvalene (TTF) derivatives; however, fullerenes form only neutral molecular complexes with BEDT-TTF (**2**)[47,48] and its twin donor **3**[49] and some others.[50,51] Hexamethoxytriphenylene (**4**),[52] having an electron-rich π system, also constructs a molecular complex with C_{60} (Chart 3). The contribution of the CT interaction does not seem to be significant. These results are due to the relatively low electron accepting properties of C_{60}.

2.2. Complexes with Traditional Hosts

2.2.1. Inclusion Complexes with Traditional Hosts

The host−guest chemistry of fullerenes with the traditional host molecules, calix[n]arenes, calix[4]resorcinarenes, and cyclotriveratrylenes, has been extensively studied for the sake of the separation and purification of fullerenes. In 1994, Atwood's[53] and Shinkai's[54] groups independently found that p-$tert$-butylcalix[8]arene (**5**) selectively precipitated with C_{60} from fullerite and thus led to an efficient purification of C_{60} (Chart 4). This discovery has resulted in many studies involving C_{60} and other calixarenes. These studies have demonstrated that the complexation depends primarily on the size of the cavity as well as the functional groups at the upper rim of the calixarene. Calix[8]-, -[6]-, and -[5]arenes (**5**,[55,56] **6**,[57] and **7**)[58−61] and oxacalix[3]arenes (**8**)[62] form a variety of inclusion complexes with fullerenes, where the guest is situated in the shallow cavity of the cone-shaped calixarene. Recently, N. Komatsu has reported that oxacalix-[3]arene derivatives **8** (R = I or Br) can serve as an efficient host for the separation of C_{60} and C_{70}.[63,64] Atwood and coworkers have also reported that cyclotriveratrilene (CTV) derivatives **9** construct a "ball-and-socket" nanostructure with C_{60} in the crystals (Figure 3).[65−67] On the other hand, calix-[4]arene (R = I or Br; **10**),[68,69] calix[4]resorcinarene (**11**),[70,71] and octaphenylcyclotetrasiloxane (**12**)[72] with relatively small cavities and/or 4-fold symmetry do not cover the fullerene molecule in the crystals. The theoretical studies clearly indicate the disadvantage of calix[4]arene derivatives, compared with other host molecules.[73−77] The results suggest that the counterbalance between fullerene/fullerene and fullerene/
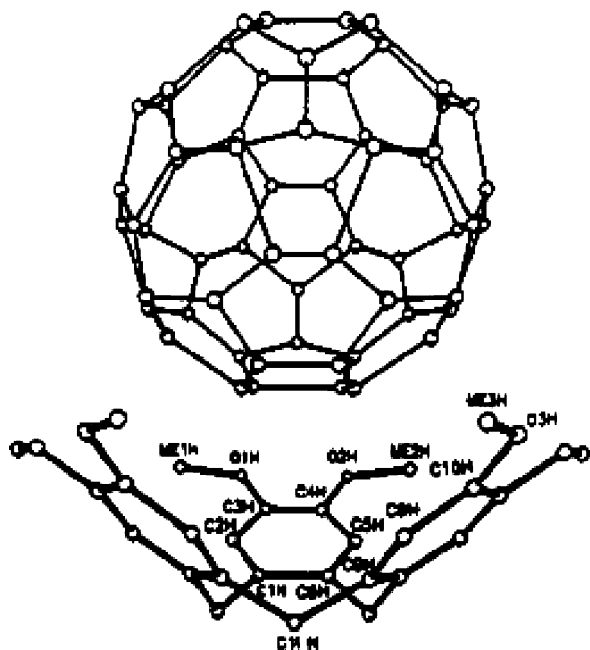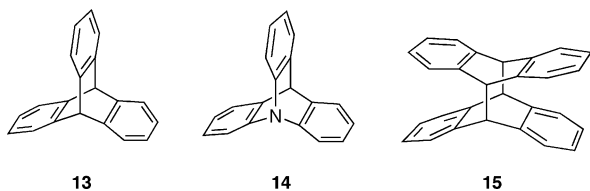
Chart 4

5: n = 8, R' = H
6: n = 6, R' = H
7: n = 5, R' = H
10: n = 4, R' = CH$_2$Ph
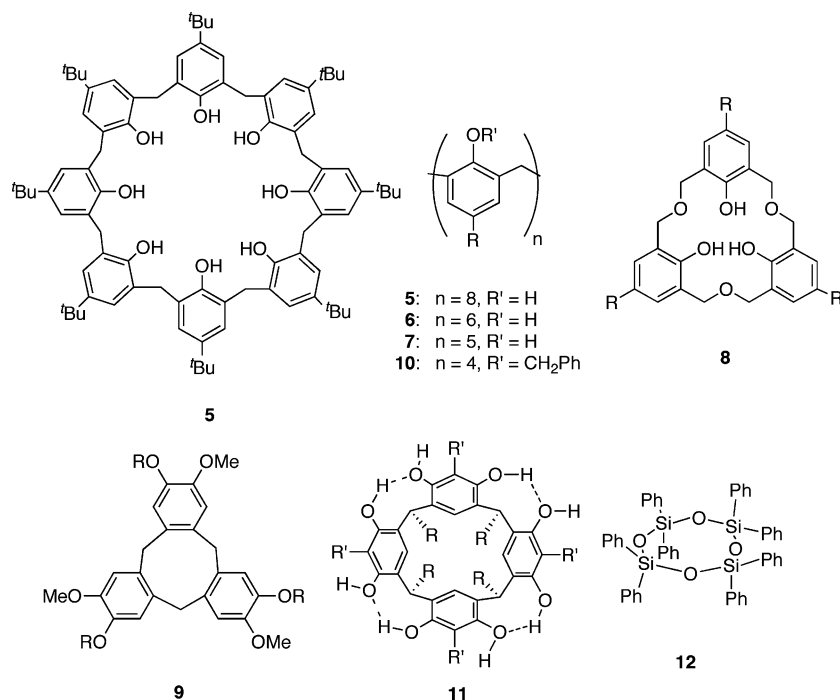
Figure 3. "Ball-and-socket" nanostructure of **9** and C_{60}. Reprinted with permission from ref 65. Copyright 1994 American Chemical Society.
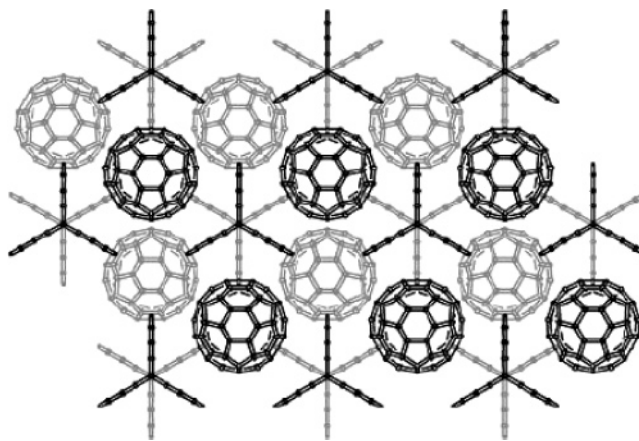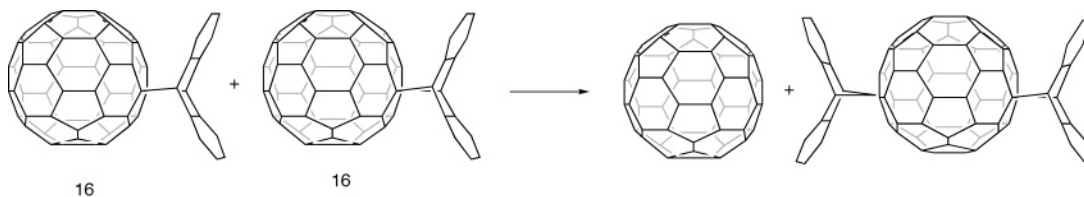
Chart 5

Figure 4. Packing arrangement for the complex of C_{60} and **14**. Reproduced from ref 78 by permission of The Royal Society of Chemistry. Copyright 1999.

Chart 6

host interactions would play an important role in the packing structure of inclusion complexes.[60,61]

Hydrocarbon molecules with a rigid framework, such as, triptycene (**13**),[78] azatriptycene (**14**),[78] and dianthracene (**15**),[79] can also form inclusion complexes with fullerenes in the solid state (Chart 5). Each C_{60} molecule is sandwiched by two molecules of **13** or **15** and is surrounded by three molecules of **14** in the crystals, which form two-dimensional layers (Figure 4). The concave shape of these molecules allows their efficient packing with the C_{60} surface to gain wide van der Waals contact.[80] Kräutler et al. reported that the 6,6-monoadduct **16** prepared from fullerene and anthracene undergoes a regiospecific thermal transformation into a solid 1:1 mixture of C_{60} and the antipodal 6,6-bisadduct **17** (Scheme 2).[81] The occurrence of this reaction can be rationalized by the specific packing of **16** in the crystal analogous to the crystal of C_{60} and **15**.

Nakamura and co-workers synthesized molecules possessing the shape of a badminton shuttlecock ($C_{60}R_5H$, **18**) and conical molecules with a fullerene apex (**19**) by the reaction of C_{60} with organocupper reagents (Chart 6).[82,83] Some

derivatives **18** bearing aryl groups on the substituents stack head-to-tail to form a one-dimensional array of fullerene molecules both in crystals and in liquid crystals; the concave surface constructed by the five aryl groups tightly binds the fullerene apex of the adjacent molecule. It is worth noting that the molecules with the long alkyl side chain **19** form a stable columnar mesophase (Figure 5).[82]

Theoretical calculations of sterically rigid macrocycles[84] predict that the concave face possesses a considerably larger negative potential than the convex surface.[85–91] These results suggest the electron negative nature of the concave surfaces of **13–19**. Together with the host properties of the calix[n]-arenes and CTVs, the rigid and sizable cavity possessing electron negative potential would be important for the high affinity for the fullerene surface.[57,65,92–96] Boyd and Reed demonstrated that graphitic and typical arene/arene distances are in the range 3.3–3.5 Å, fullerene/arene approaches lie in the range 3.0–3.5 Å, and fullerene/fullerene separations are typically ~3.2 Å.[97] The close approach is proposed to reflect an attractive π–π interaction. The interaction was interpreted with the "Hunter–Sanders rule".[98–102] On the

Scheme 2

Figure 5. Nanoshuttlecock molecule **19** and a 3D model of a stack of five molecules.
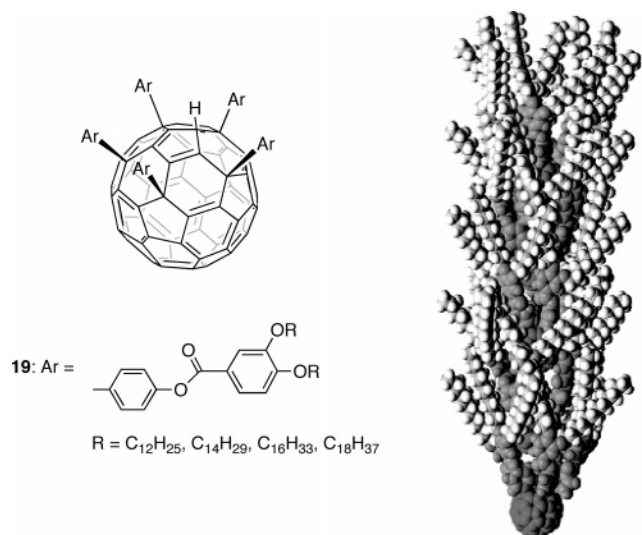
basis of recent experimental studies, Raston proposed that the frequently observed short distance is ascribed to the polarization of fullerene in the crystal packing.[72,92−96]

2.2.2. Complexation with Traditional Host Molecules in Solution

The first example of C_{60} involved in macrocyclic host molecules in solution was reported by Ringsdorf, Diederich, and co-workers in 1992. They found that fullerenes are incorporated into the lipophilic cavity of azacrown ethers **20** and **21** (Chart 7).[103] Shortly thereafter, Wennerström and co-workers reported a water-soluble complex between γ-cyclodextrin (γ-CD, **22**) and C_{60}.[104−108] The stoichiometry was determined to be 2:1.[109] This discovery led to extensive studies on various CD complexes related to water-soluble fullerene complexes,[110−115] tools for nanocomposites,[116−118] and a novel reducing reagent.[119−123] Geckeler and Constabel first reported that [7]cucurbiturea forms a complex with C_{60} by a solid−liquid reaction.[124] In these complexes, attractive interactions between the heteroatoms (as n-donors) and the fullerene surface are operative,[109,125] but the main driving force of these complexes is the hydrophobic effect.

As mentioned above, alkyl- or halogen-substituted calix-[4]-, -[6]-, and -[8]arenes readily form inclusion complexes with fullerenes in the solid state. However, the binding ability of these complexes in nonpolar organic solvents is
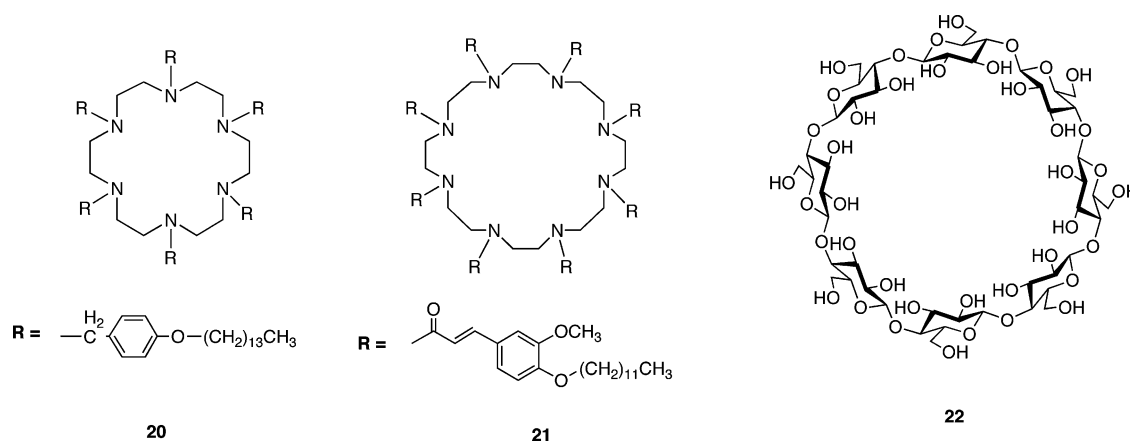
generally poor.[58−61,75,78−80,126,127] On the other hand, Fukazawa and co-workers first found that OH-unsubstituted calix[5]-arenes **23a−c** form rather stable complexes in solution (Chart 8).[128] The association constants of iodo derivative

Chart 8

23a: R = R' = H
23b: R = R' = Me
23c: R = Me, R' = I
23d: R = R' = -allyl
23e: R = R' = -CH₂Ph
23f: R = R' = -Ph
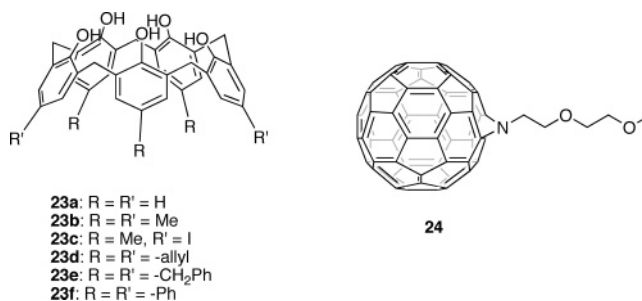
23c[128] and phenyl derivative **23e**[133] are in the range $2-3 \times 10^3$ dm³ mol⁻¹ (Table 1). Owing to the C_{5v} cone conforma-

Table 1. Association Constants (K_a, dm⁻³ mol⁻¹) of Selected Calixarenes and C_{60} at 25 °C in Toluene

calixarene	K_a	ref
23a	30 ± 2	126
23b	1673 ± 70	128
23c	2120 ± 110	128
23d	292 ± 15	126
23e	2800 ± 200	132
23f	3000 ± 200	133
25 (R = ^{t}Bu)	676 ± 28	136
26 (R = ^{t}Bu)	296 ± 9	138
8 (R = ^{t}Bu)	35.6 ± 0.3	62

tion, the cavity size and curvature are complementary to fullerenes.[128−133] They have also studied the binding properties between **23b** and a fullerene derivative **24** based on their thermodynamic parameters.[134,135] Remarkable solvent effects between toluene and chloroform were observed; in toluene the entropy changes in the complex formation are all positive, but in chloroform they are all negative. These results indicate that the extensive desolvation from the fullerene moiety of these compounds plays an important role in the guest inclusion process. Georghiou and co-workers prepared calix-[4]naphthalene (**25**)[136,137] and trioxacalix[3]naphthylene (**26**)[138] derivatives (Chart 9). These hosts afford more stable complexes than the corresponding calixarenes (Table 1), probably due to the deep cavities and the high affinity of the naphthylene units for fullerene. These results exclude
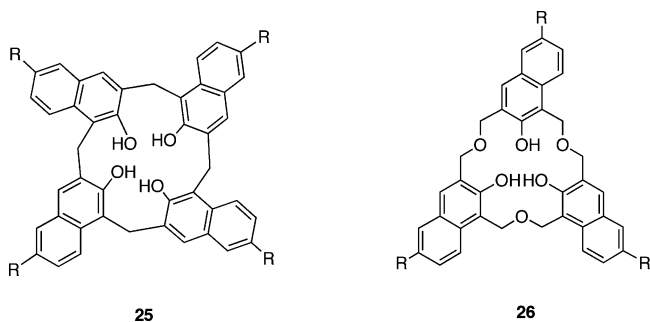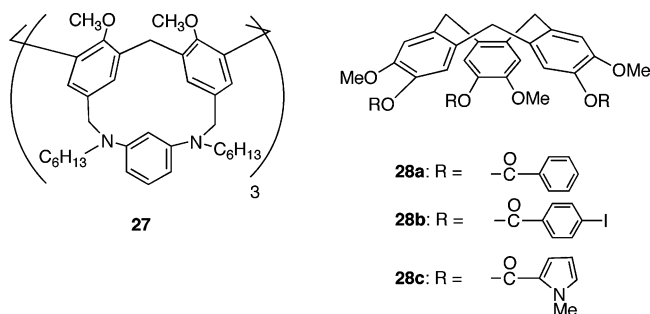
Chart 7

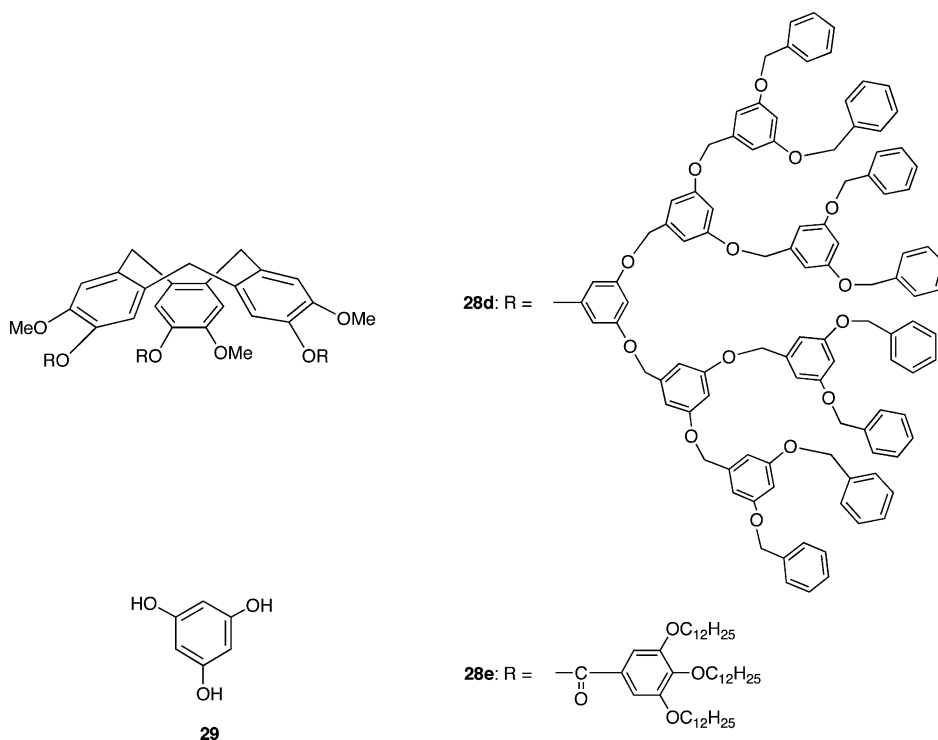**R =**

R =

20

21

22

Chart 9

25

26

Chart 10

27

28a: R = (benzoyl)

28b: R = (4-iodobenzoyl)
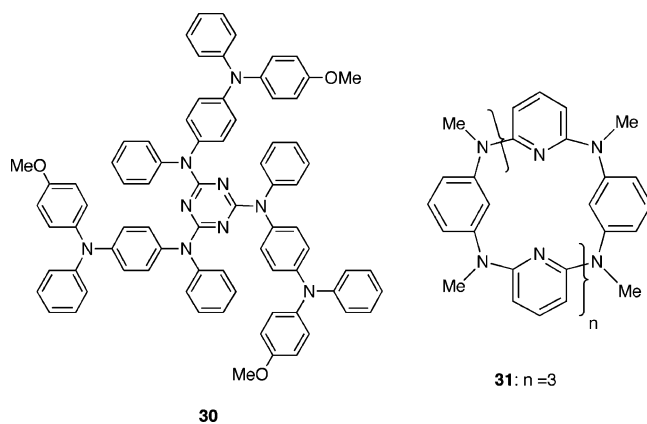
28c: R = (N-methylpyrrole carbonyl)

To prepare host molecules with high affinity for fullerenes, Shinkai and co-workers first designed calix[6]arene derivatives bearing electron-rich aniline or 1,3-diaminobenzene units, expecting that the CT interaction would act as a driving force. The association constants (K_a) of **27** (Chart 10) for C_{60} increased to 1.1×10^2 dm^3 mol^{-1}.[73,76] Matsubara and co-workers applied this consideration to the synthesis of CTV derivatives **28a−c**, having N-methylpyrrole or benzoyl pendants. The CTVs **28** formed fairly stable complexes with fullerenes; particularly, the K_a value of **28c** for C_{60} is 4.8×10^4 dm^3 mol^{-1}.[139] Nierengarten and co-workers have also found that CTV derivatives **28d** (Chart 11) functionalized by Frechet-type dendrons can act as hosts for fullerenes.[140] The K_a values are significantly increased as the generation number of the dendric substituents is increased. The Frechet-type dendrimers can provide a space size comparable with that of C_{60}. A C_{60} complex of the CTV **28e** with 18 long alkyl chains prepared by Nierengarten's group has mesomorphic properties.[141] Shinkai's group independently found the host properties of the dendrimers with phloroglucinol (**29**) and tetraphenylporphyrin cores for C_{60}. But the K_a values of these dendrimers are not so high (<100 dm^3 mol^{-1}).[142]

As expected, a dendrimer **30**[143] and a calixarene **31**[144] based on triarylamine units (Chart 12) can serve as efficient hosts for fullerenes. The presence of a fullerene quenches the intense fluorescent emission of these host molecules very effectively. Then, the stability of the complexes is evaluated by the Stern−Volmer constants (K_{SV}). Although the K_{SV} values are not direct measures of the complexation because of the quenching mechanisms, they would be informative to estimate the relative stability of these complexes. Table 2 lists the K_{SV} values of the complexes. The stability of complexes of **31** is considerably higher than that of the corresponding calixarenes.

Fukazawa and co-workers have found that the calix[5]-arene **23b** forms a 1:1 complex in solution, but it forms a 1:2 complex in the solid state.[145] In the case of benzyl and

the possibility of the disadvantageous effect of C_4 molecular symmetry on binding to fullerenes.

2.3. Designed Host Molecules

2.3.1. Based on Traditional Host Molecules

As mentioned above, the binding abilities of the traditional concave hosts are not so high. The progress of the studies prompted the synthetic chemists to prepare well-designed host molecules for fullerenes. These host molecules possess a sizable bowl-shaped, cage-shaped, or belt-shaped cavity.

Chart 11

28d: R =

28e: R =

29

Chart 12

30

31: n =3

Table 2. Stern−Volmer Constants (K_{SV}, $dm^{-3} mol^{-1}$) of 31, 32, and Fullerenes at 27 °C in Toluene

compd	fullerene	K_{SV}	ref
30	C_{60}	180000 ± 8000	143
31	C_{60}	70680 ± 2060	144
31	C_{70}	136620 ± 3770	144

Chart 13

32

32a: X =

32b: X =

32c: X =

33

R =   X =

Chart 14

34a: X =

34b: X =

35a: X =

35b: X =

32a bearing a 1,3-diethynylphenylene tether afforded considerably stable complexes with fullerenes.[146] The theoretical calculation exhibits the encapsulated structure to gain the wide contact area between the host and guest. Gutsche and co-workers have also synthesized several calixarene dimers based on calix[5]- or -[6]arenes.[126] Moreover, Parados and co-workers prepared a calix[4]arene dimer.[147] In comparison with these calixarene dimers, the calix[5]arene dimer **33** shows the high affinity for C_{60}.[126] The results clearly indicate the efficiency of the calix[5]arene framework. Yamamoto and co-workers prepared CTV dimer hosts **34** and **35** (Chart 14).[148,149] The association constants of these cage-shaped host molecules for fullerenes are up to 10^5 (Table 3). Fukazawa's

phenyl derivatives **23e** and **23f**, 1:2 complexes are formed in toluene solution.[132,133] The crystallographic analyses of **23b** and **23f** reveal that one C_{60} molecule is sandwiched by two calix[5]arene cavities (Figure 6). A CTV derivative **28a**[139] and oxacalix[3]naphthalene **26** (R = ^tBu)[138] also form 1:2 complexes in the solid state. From the molecular structure of **23b**, Fukazawa designed new host molecules **32** with a calix[5]arene dimer structure (Chart 13). The host molecule

Figure 6. Space filling projection of **23f**·C_{60}. Reproduced from ref 133 by permission of The Royal Society of Chemistry. Copyright 2002.

Table 3. Association Constants (K_a, dm^{-3} mol^{-1}) of Cage-Shaped Host Molecules 32−35 and Fullerenes at 25 °C in Toluene

compd	K_a for C$_{60}$	K_a for C$_{70}$	ref
32a	76000 ± 5000	163000 ± 16000	146
32b	8300 ± 200	85000 ± 13000	146
32c	2700 ± 100	5500 ± 200	145
33	1300 ± 65	625 ± 32	126
34a	23600 ± 100		148
34b	23000 ± 390		148
35a	19100 ± 110	26500 ± 260[a]	149
35b	5200 ± 90	15400 ± 100[a]	149

[a] In benzene.

group structurally modified the calix[5]arene dimer to serve as a fluorescent sensor[150] and supramolecular nanonetworks.[151]

Macrocyclic compounds **37** and **38** (Chart 15) bearing ether oxygen atoms synthesized by Yoshida and co-workers form rather stable complexes with C$_{60}$ (**37**, K_a = 3410 ± 1510 dm^{-3} mol^{-1}; **38**, K_a = 5430 ± 370 dm^{-3} mol^{-1} in toluene).[152] A cavitand **39** with a deep cavity was prepared by Rebek's group. The association constants of **39** for fullerenes are not so large (K_a for C$_{60}$ = 900 ± 250 dm^{-3} mol^{-1} in toluene), but the sele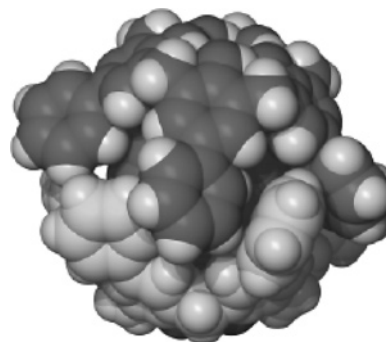ctivity between C$_{60}$ and C$_{70}$ is relatively high, probably due to the rigidity of the cavity.[153,154] Some cage-shaped host molecules constructed by coordination bonds of transition metal ions have been examined for the encapsulation of fullerene. Shinkai's group first reported a C$_{60}$ complex with a self-assembled cage, the oxacalix[3]-arene dimer **40** cross-linked by three Pd(II) complexes **41** (Scheme 3).[155−157] Claessens and Diederich co-workers also described self-assembled cage-shaped molecules based on two subphthalocyanine units[158] and two cavitand units,[159]
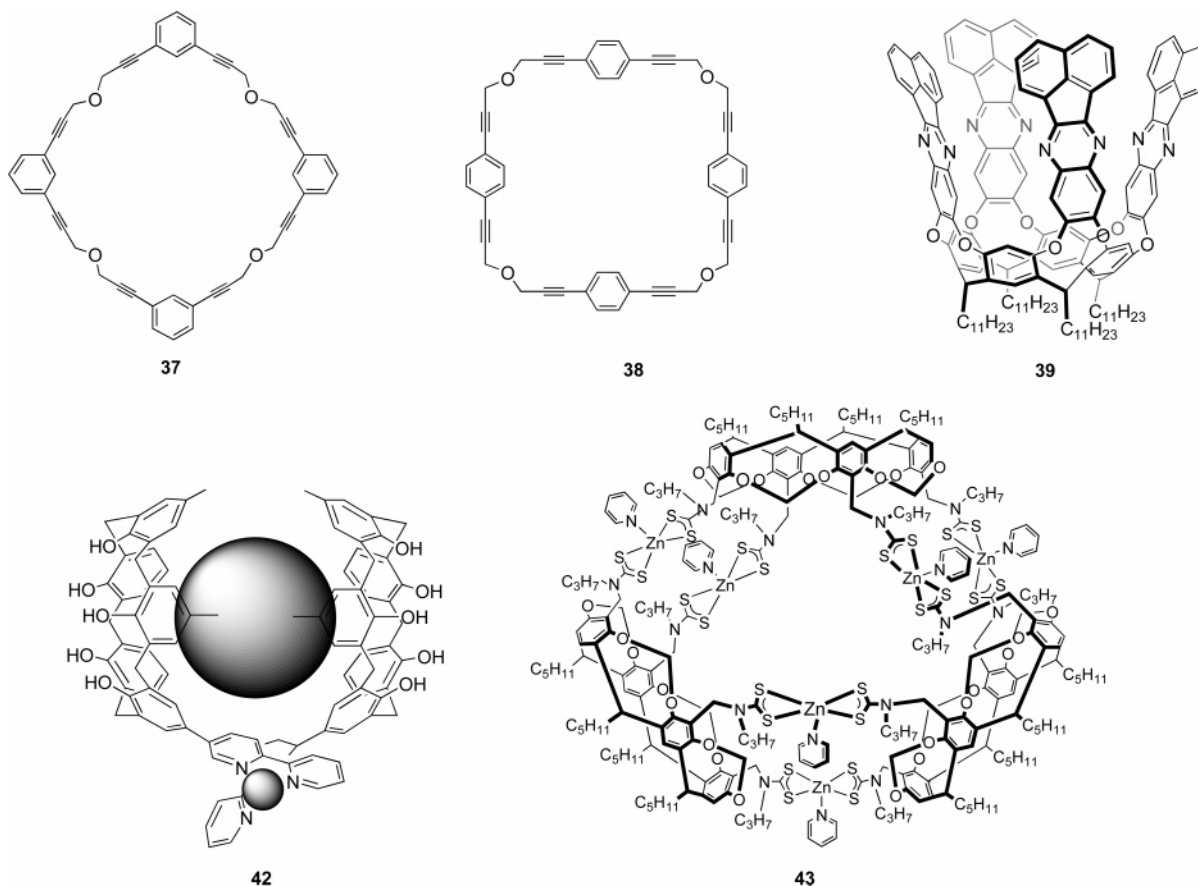
respectively. Calix[5]arene derivatives prepared by Fukaza-wa's group construct the dimeric structure **42** in the presence of silver(I) or copper(II) ions to catch a C$_{60}$ molecule in the resulting cavity.[160,161] These cage compounds involving metal cation(s) show relatively small association constants, probably due to the high molecular mobility. A calixresorcinol-based metal-assembled host **43** with a rigid and sizable cavity forms extremely stable inclusion complexes with fullerenes (K_a > 10^5 dm^{-3} mol^{-1}).[162,163]

2.3.2. Based on Porphyrin Derivatives

The cocrystals of C$_{60}$ with chromium(II) porphyrin[164] and octakis(dimethylamino)porphyrazine[165] were reported in 1991 and 1995. The basis of the complexation was proposed to be a CT interaction. In 1997, Boyd, Reed, and co-workers first pointed out a close contact (∼2.7 Å) between the porphyrin and C$_{60}$, suggesting an attraction of C$_{60}$ to the center of a porphyrin ring.[97] In the past decade, a number of articles have shown that porphyrin derivatives cocrystallize with C$_{60}$.[166−175]

Reed, Boyd, and co-workers found that acyclic ("Jaws") bisporphyrins **44** and **45** are employed as efficient hosts for fullerenes (Chart 16).[176,177] The X-ray structures of these complexes reveal that the electron-rich 6:6 ring-juncture bonds of C$_{60}$ show an unusually close approach to the porphyrin planes (Figure 7). The association constants in toluene solution span the range 490−5200 dm^{-3} mol^{-1}. It is noteworthy that the variable temperature ^{13}C NMR spectra reveal the coalescence of two fullerene signals corresponding to rapid exchange between the complexed and uncomplexed fullerenes at −55 °C for **44·**C$_{60}$.[176] The association constants and coalescence temperatures vary with the metal ion of the

Chart 15

37

38

39

42

43

Scheme 3

40

41

6CF$_3$SO$_3^-$

6CF$_3$SO$_3^-$

Chart 16

44

45a: R = H, X =

45b: R = H, X =

46: R = OCH$_3$, X =
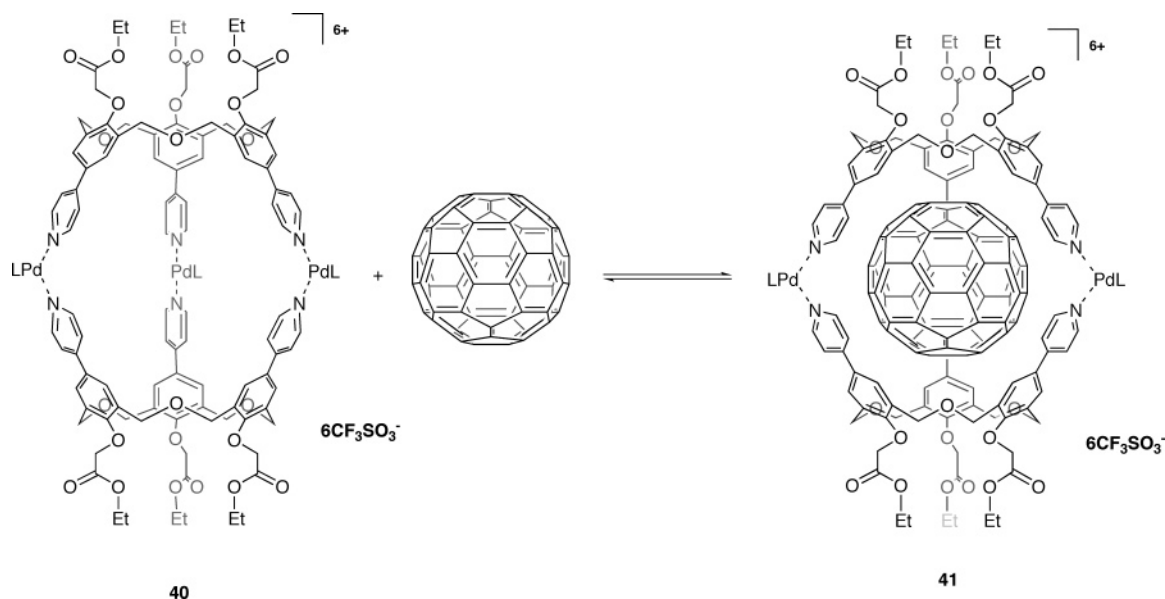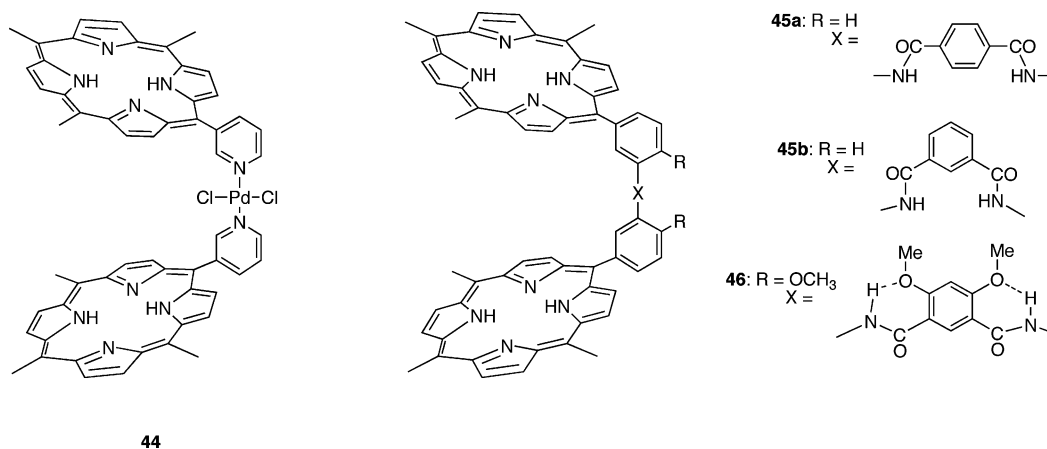
host and the structure of the tether.[177] The bisporphyrin receptors **46** with the preorganized U-shaped feature exhibit considerably strong binding abilities with fullerenes in solution (~3.4 × 10^8 dm^{-3} mol^{-1}).[178] A number of bisporphyrin[179−181] and multiporphyrin[182−184] receptors have been developed, and the resulting porphyrin−fullerene assemblies have brought forward many interesting photophysical, photochemical, and electrochemical properties.[185−188]

Aida and co-workers independently found that a face-to-face cyclic dimer of zinc porphyrins **47**−Zn forms a highly stable 1:1 inclusion complex with C$_{60}$. The K_a value (6.7 × 10^5 dm^{-3} mol^{-1}) exceeds those of the acyclic bisporphyrins.[189] The molecular structure of **47**−Zn reveals that one 5:6 ring fusion is located on the central metal ion.[190] Among several metal complexes, **47**−RhMe exhibits the highest affinity toward C$_{60}$ (2.4 × 10^7 dm^{-3} mol^{-1}) and C$_{70}$ (about 10^8 dm^{-3} mol^{-1}) in benzene. With respect to the high affinity, the coalescence of the NMR signals corresponding to in-and-out motion of the guest was not observed even at 100 °C.[191] They have also synthesized a series of cyclic porphyrin dimers with various cavity sizes to create tailor-made hosts for higher fullerenes and a fullerene dimer.[192−194] A porphyrin dimer **48** with adjustable linkers involving disulfide units was prepared by Sanders and co-workers (Chart 17).[195]

There is an unexpectedly strong interaction between the curved π surface of C$_{60}$ and the flat π surface of porphyrins.

Chart 17

47: R = -(CH$_2$)$_6$-
48: R = -(CH$_2$)$_2$-S-S-(CH$_2$)$_2$-
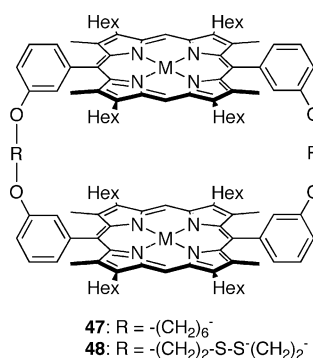
Recent theoretical[196] and experimental[174] studies suggest that the considerably strong π−π interaction is largely the result of van der Waals dispersion force and is enhanced by weak electrostatic interaction. The conclusion would be compatible with the other fullerene complexes, as shown above. The supramolecular chemistry of fullerenes would be understandable if they possessed a positive electronic potential of the convex surface.[19] However, these studies have provided the information of the convex π surface of fullerenes alone. C$_{60}$ can be regarded as a special molecule with a highly symmetric π system; the electrostatic difference between 5:6 and 6:6 fusions is characteristic of the fullerene surface. On

Figure 7. Molecular structure of **44**·C_{60}. Reprinted with permission from ref 176. Copyright 2000 American Chemical Society.

the other hand, it has been known that the supramolecular properties of carbon nanotubes are similar to those of fullerenes; porphyrin[197,198] and pyrene[199,200] derivatives bind to the convex surface of carbon nanotubes, though carbon nanotubes have few 5:6 fusions in the π system. To explore the substanti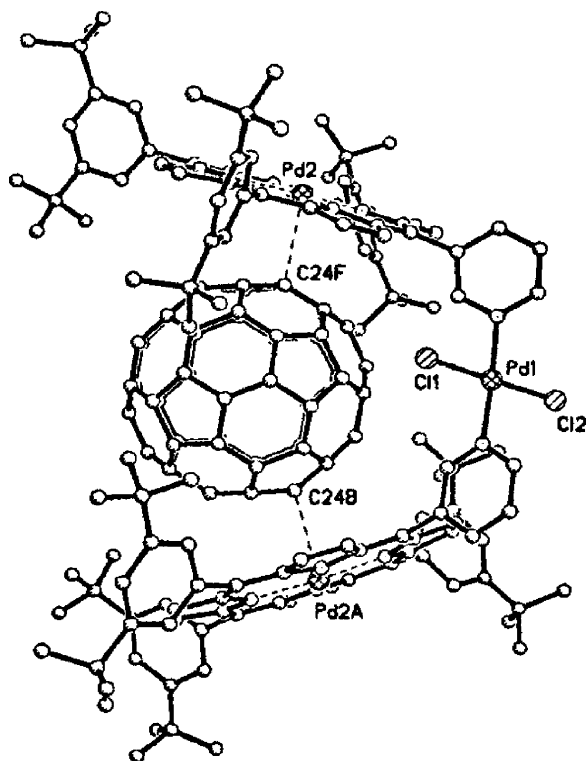al properties of curved conjugated systems, good model compounds with a bowl-shape or belt-shape cavity surrounded by p orbitals are needed.

3. Bowl-Shaped Conjugated Systems

3.1. Stacking Structure

Corannulene (**49**), synthesized by Barth and Lowton in 1966 (Scheme 4), has been known as the first bowl-shaped conjugated system.[201,202] The discovery of fullerenes has prompted a general interest in bowl-shaped aromatic hydrocarbons. In this context, simple and practical syntheses of **49** have been developed by Scott's, Rabideau's, and Siegel's groups. The methods are applicable to the synthesis of a variety of bowl-shaped conjugated systems.[203–215] This review only deals with the studies concerning the concave–convex π–π interaction. Details of the chemistry are described by Scott's review in this issue.[216]

If the two surfaces exert some level of attraction toward one another, bowl-shaped conjugated systems would favor a stacking structure in a concave–convex fashion. X-ray analysis of **49**, however, shows the absence of any amount

Scheme 4

a)   b)
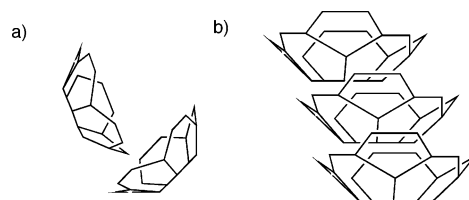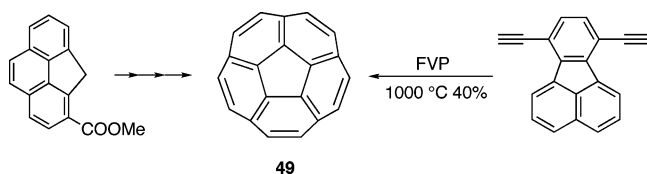
Figure 8. Crystal packing of (a) **49** and (b) **50**.

Chart 18
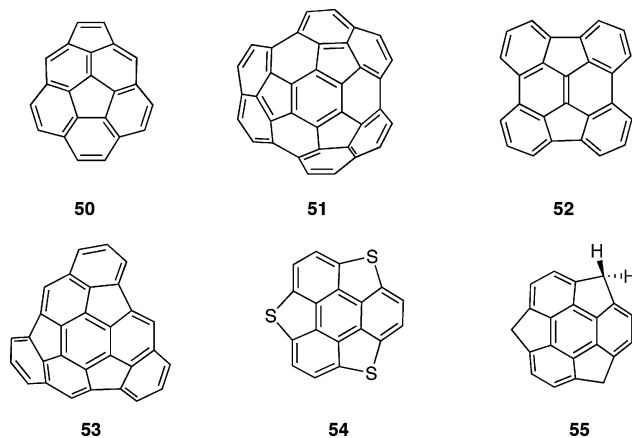
of bowl-stacking (Figure 8a).[217,218] Rabideau and co-workers have prepared cyclopentacoannulene (**50**)[219] and found that the additional five-membered ring leads to bowl-stacking in the crystal (Figure 8b). While **49** undergoes rapid bowl-to-bowl inversion in solution (10–11 kcal mol^{-1}), **50** (Chart 18) is locked into the bowl shape, at least on the NMR time scale. The X-ray crystal structure of **50** also indicates that the additional five-membered ring produces a significant increase in curvature relative to **49**. Both molecular rigidity and increasing bowl depth would play important roles in the construction of bowl-stacking in crystals.[219] Scott and co-workers have synthesized circumtriindene ($C_{36}H_{12}$, **51**), with the deepest cavity, by flash vacuum pyrolysis (FVP).[220,221] In the solid state, **51** forms linear stacks, as expected (Figure 9). This packing produces rather close C···C contacts between the rim of one bowl and bottom of the adjacent bowl.[222] A family of bowl-shaped conjugated systems with
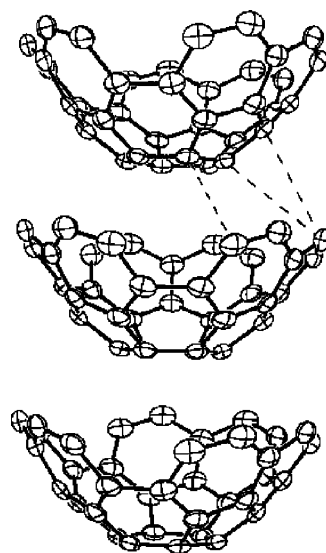
Figure 9. Crystal packing of **51**. Reprinted with permission from ref 222. Copyright 1997 American Chemical Society.
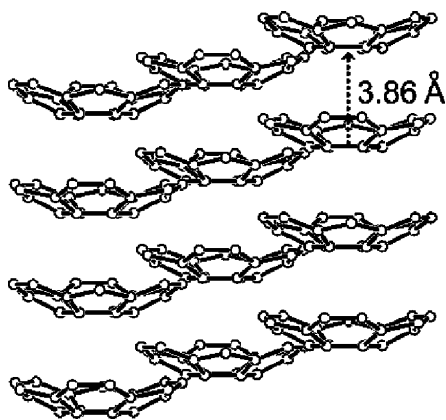
Figure 10. Crystal packing of **55**. Reprinted with permission from ref 230. Copyright 2005 American Chemical Society.

bowl-stacking in the solid state have begun to appear in recent years, i.e., diindenocrysene ($C_{26}H_{12}$, **52**),[223] hemifullerene ($C_{30}H_{12}$, **53**),[224−227] triphenylenotrithiophene (**54**),[228] and sumanene (**55**).[229,230] The stacks of **51**, **54**, and **55** (Figure 10) are aligned in one direction. Thus, the dipoles of all bowls are also aligned, so these crystals should exhibit pyroelectric properties. These findings strongly suggest the potential utility of curved conjugated systems as electrically active materials in the solid state.[222,228]

3.2. Host Properties

Some cyclophane-type host molecules bearing bowl-shaped conjugated systems have been designed. Siegel and co-workers have prepared corannulene-based cyclophanes **56**−**58** (Chart 19),[231,232] and Boldwell and co-workers have synthesized a series of (2,7)pyrenophanes with increasingly nonplanar pyrene moieties (**59**).[233−239] Although these compounds exhibit few host properties for organic molecules, their synthetic methodologies will open the way to create cyclophanes with novel host properties in the near future.

Corannulene (**49**) forms a stable complex with $(C_{60})^+$ in the gas phase.[240] This result indicates that the curved π surfaces of C_{60} and corannulene (**49**) are geometrically well matched. However, unsubstituted **49** shows no evidence of complexation with fullerenes in solution as well as in the

Chart 19

Chart 20

60a Ar = ⎯⟨benzene⟩⎯OMe

60b Ar = ⟨naphthalene⟩

61

Chart 21

62

63
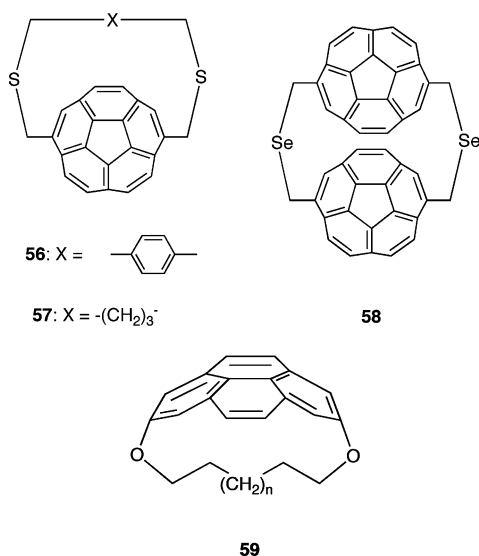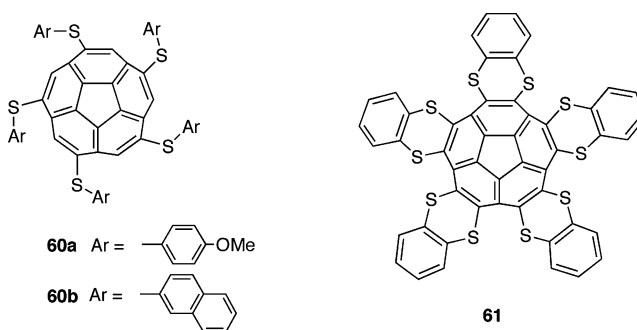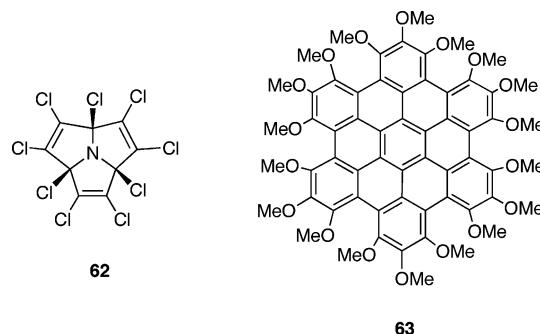
solid state. Georghiou, Scott, and co-workers have designed and synthesized corannulene derivatives **60**[241] and **61**[242] (Chart 20) for inclusion of fullerene molecules. The association constants (K_a) of the C_{60} complexes of arylthio derivatives **60a** and **60b** are ∼300 and ∼60 $dm^{−3} mol^{−1}$ in toluene, respectively, and the K_a values for the C_{60} complexes of **61** with expanded π systems are ∼1400 $dm^{−3} mol^{−1}$. These results clearly indicate the importance of the electronic effects of substitutents on the binding of fullerene in solution. Mascal, Balch, and co-workers have reported that hexachloroazatriquinacene (**62**), with a bowl-shaped structure (Chart 21), affords an inclusion complex with C_{60}, but they suggest the importance of the interaction between halogen atoms and the fullerene surface.[243] Müllen and co-workers have also found that a hexabenzocoronene derivative (**63**) with a double-concave structure forms an inclusion complex with C_{60}. The fullerene is positioned exactly on the central benzene rings of **63**, thus yielding a perfect columnar packing arrangement.[244]

Siegel and co-workers have studied the electronic properties of some curved aromatic hydrocarbons theoretically, and they predicted that these compounds would be polarized because of the unsymmetrical nature of their π orbitals.[245,246] Scott and co-workers have also studied the electrostatic potential on the surface of curved aromatic hydrocarbons by using DFT calculations.[213] According to the prediction, the concave surface shows the more negative electrostatic potential, and cation−π complexation should be favored inside the bowl rather than outside, in the absence of overriding steric factors.[247,248] They found the first experimental evidence for the complexation to circumtrindene **51** in solution. However, this stereochemical assignment has not yet been confirmed experimentally.[249] Contrary to their results, Sastry and co-workers have reported theoretical studies on the cation−π interactions of sumanene **55**; the convex binding is more favorable compared to that of the concave side when the 6-331+G** basis set is employed.[250,251] The results of theoretical calculations have as yet been controversial.

Chart 22

64

65

Chart 23

66

67
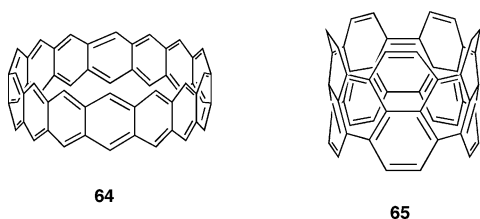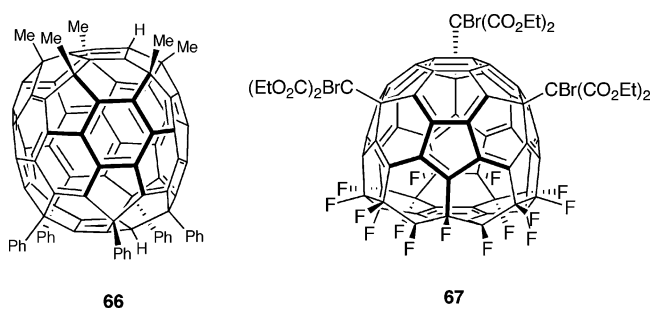
As described above, no bowl-shaped conjugated systems form fullerene complexes in solution except Scott's and Georghiou's corannulene derivatives **60** and **61**. Even in these compounds, the π system of the substituents would play an important role in the relatively strong binding to fullerenes. Thus, the studies lead to the conclusion that the attractive force of the concave–convex π–π interaction is not so significant, if at all. On the other hand, it has been known that the wide contact is important for the self-aggregation behavior of porphyrins,[98] velcraplexes,[252–254] and size persistent macrocycles.[255] Compared with these van der Waals complexes, the number of short contacts between the host and guest presented here seems not enough. In this context, host molecules bearing a sizable cavity are needed to explore the concave–convex π–π interaction substantially.

4. Belt-Shaped Conjugated Systems

4.1. Cyclacene and Related Compounds

Before discovery of fullerenes, belt-shaped conjugated systems, in which the p orbitals are aligned horizontally on a rigid surface, had already been regarded as attractive synthetic targets because of their geometrical beauty. These compounds may be termed "carbon nanorings", and they will serve as good model compounds for carbon nanotubes upon their discovery. Cyclacenes **64**[256–270] and the related compounds **65**[271–274] are representative of the family (Chart 22). Although several chemists have attempted cyclacene synthesis, their efforts have resulted in failure.
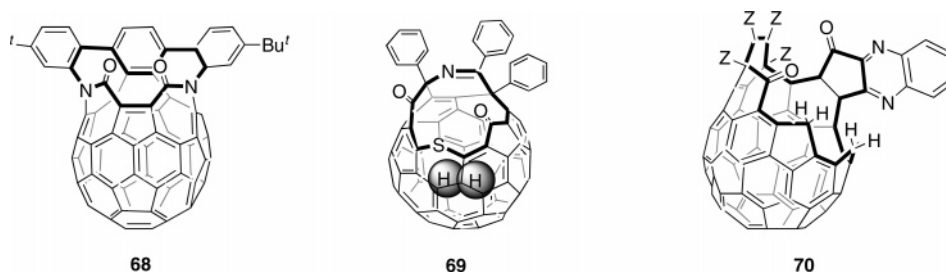
Recently, new approaches to synthesize belt-shaped conjugated systems starting from fullerenes have provided fruitful results. Nakamura and co-workers first synthesized [10]cyclophenacene derivatives **66** through selective penta-addition of a methylcopper reagent followed by addition of a phenylcopper reagent to a suitably modified synthetic intermediate.[275,276] Moreover, synthesis of "emerald green fullerene" (**67**; Chart 23) was reported by Taylor and co-workers.[277] The first [18]trannulene derivative (**67**) was achieved by novel S_N2'' substitution reaction of anionic diethyl 2-bromomalonate replacing three fluorine atoms of $C_{60}F_{18}$. These approaches have furnished a variety of curved conjugated systems.[278–287] However, the lack of a cavity in these compounds is unavoidable, owing to the synthetic method.

4.2. Open-Cage Fullerenes

In this context, open-cage fullerenes are of great interest for the creation of new host molecules with a large π pocket. Recently, Rubin's,[288–293] Komatsu's,[294–301] Iwamatsu's,[302–309] and other's[310–312] groups have created various open-cage fullerenes (**68**–**70**) by the "operation" on C_{60} and C_{70}. The host molecules can incorporate a small guest such as a He atom[291] or H_2[291,296,308] and H_2O[306,308] molecules into the deep cavity (Chart 24). The operation methods may be applicable to higher fullerenes or carbon nanotubes to produce host molecules possessing a large cavity.[313]

4.3. Cyclocarbon, Cyclo-*para*-phenylene, and the Hybrid Compounds

The cyclocabons **71** (Chart 25)—their generation has been confirmed by Diederich and Rubin, and Tobe—are intriguing species as important intermediates in the formation mechanisms of fullerene.[314–319] However, the cyclocarbons are obviously not appropriate for evaluating the host properties because of their high reactivity.

The first synthetic challenge toward cycloparaphenylene **72** was reported by Vögtle and co-workers.[320] However, attempted syntheses of cyclophane-type precursors such as **73** failed. On the other hand, Herges' group has found that tetradehydrodiacthrace (TDDA; **74**) reacts with a number of alkenes upon photoirradiation to form cycloparaphenylene-related compounds through metathesis of the corresponding [2+2]cycloadducts. Thus, TDDA (**74**) reacts with itself and forms a "picotube" **75** with a tubelike structure (Scheme 5),[321–324] and several belt-shaped conjugated systems (**76**,[325] **77**,[326] and **78**)[325] were also obtained by using **74** as a starting material. Moreover, they have successfully synthesized the

Chart 24

68

69

70

Chart 25

Cyclocarbon
71

Cycloparaphenylene
72

73

74

76

77

78

79

Scheme 5

74   **74**

$h\nu$
qualtz
C_6H_6

picotube
75

Scheme 6

81

[CpCo(CO)₂]
$h\nu$

80
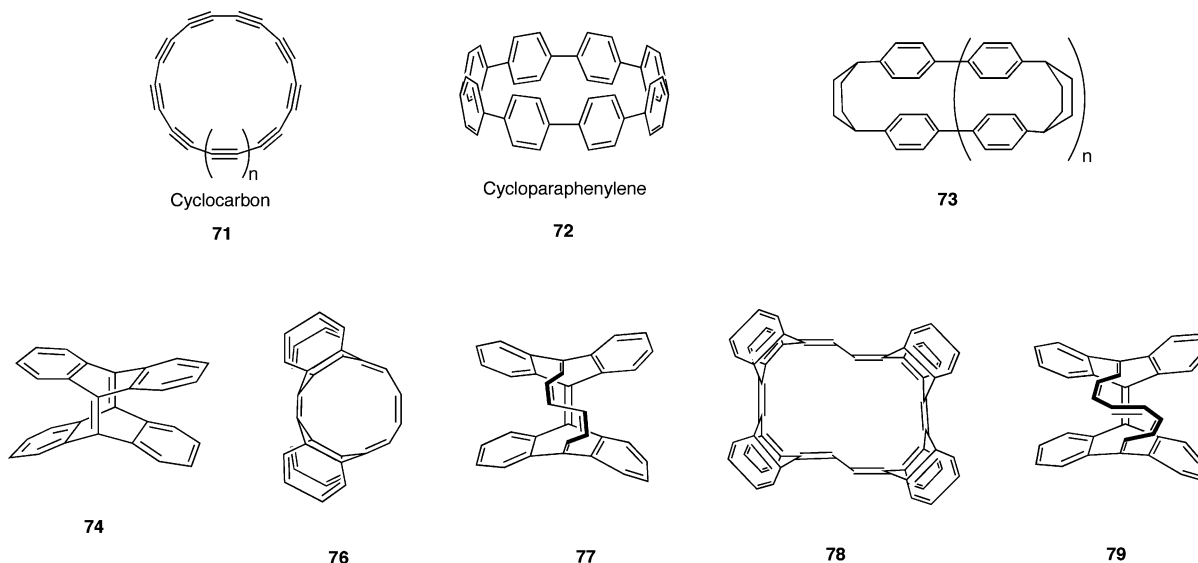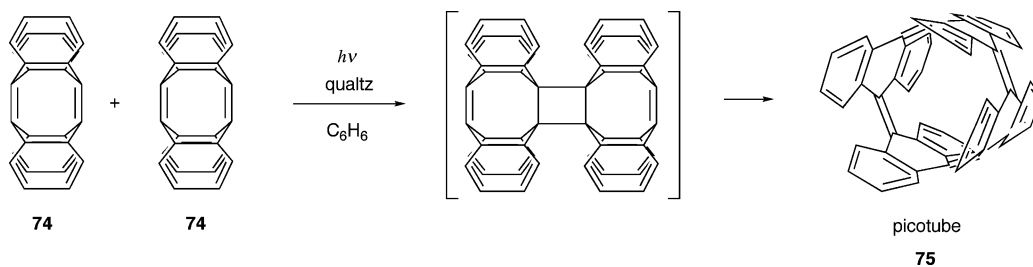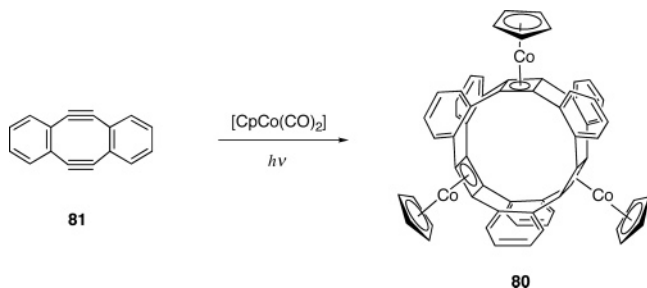
first stable Möbius aromatic compound (**79**) by employing their synthetic methodology.[327−330] Gleiter and co-workers synthesized metal complexes of a belt-shaped π system (**80**) by the reaction of dibenzocyclooctadiyne **81** with [CpCo-(CO)₂] derivatives (Scheme 6).[331] However, the cavity sizes of these compounds are not long enough to include the fullerene.

The hybrid between cyclocarbons and cyclo-*para*-phenylenes presents a variety of unique molecular designs; all the compounds are predicted to possess a belt-shaped structure. The family of compounds may be termed paracyclophynes.[332−334] In view of the known reactivity of polyynes, it is expected that the shortening of the sp carbon chains of cyclophynes would increase their kinetic stabilities. Haley and co-workers attempted to prepare [8₂]paracyclophyne (**82**; Chart 26) by oxidative decomplexation of the corresponding cobalt complex precursor **83**. However, all the products were elusive.[335] On the extension of the cyclocarbon chemistry, Tobe and co-workers also examined the generation of highly strained paracyclophynes, [12₂]-paracyclophyne (**84**)[336] and [6ₙ]paracyclophynes (**85**).[337] Although these cyclophynes were not isolable, laser irradiation of the corresponding precursors **86** and **87** produced the negative ions of these cyclophynes by extrusion of the indan fragments, which were detected by laser-desorption time-of-flight (LDTOF) mass spectrometry (Scheme 7). The next

Chart 26

82: n = 1
84: n = 3

83

86

Scheme 7

87: n = 3~6

laser irradiation or $h\nu$

85: n = 3~6

Scheme 8

89

1) aq. HCl, THF, rt,

2) BuMe$_2$SiOTf
Et$_3$N, CH$_2$Cl$_2$,

3) $h\nu$, C$_6$H$_6$, 12 °C

15 Å

R = CH$_2$OSiMe$_2$tBu
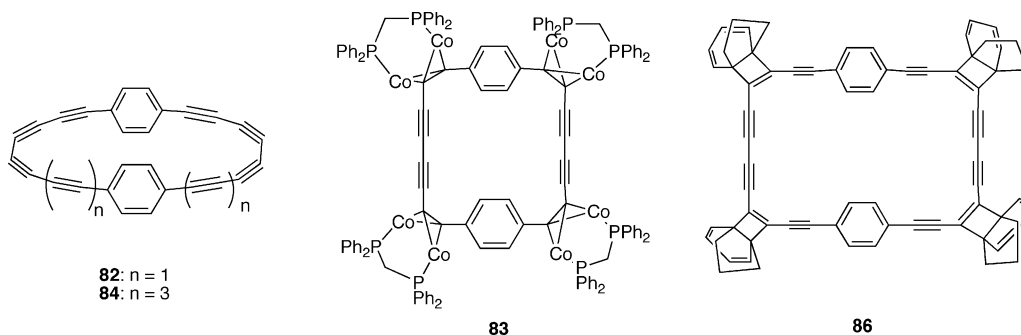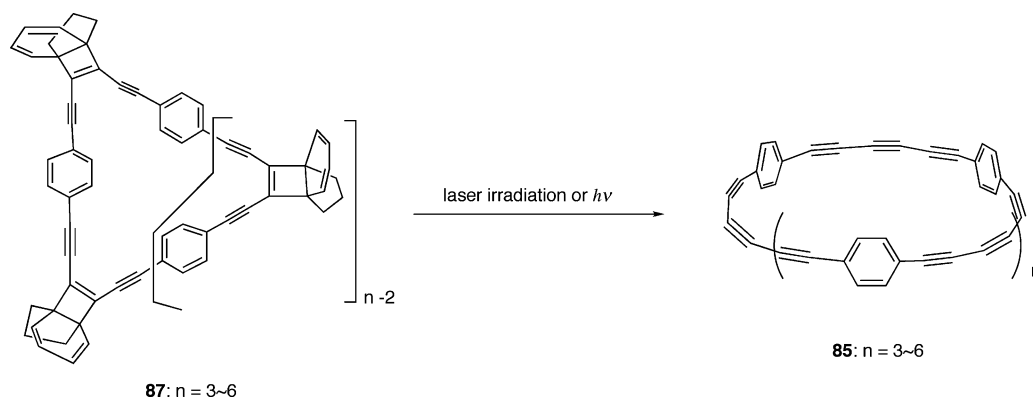
88
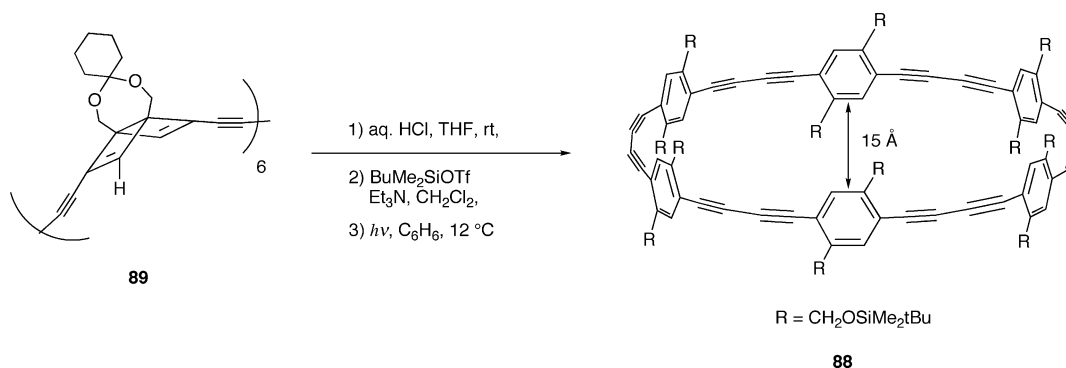
shorter homologue, a butadiyne-bridged [4$_6$]paracyclophyne derivative (**88**), was synthesized by Ohkita and Tsuji by using photochemical valence isomerization of the corresponding Dewar benzene valence isomer **89** (Scheme 8).[338–340] According to the theoretical calculation (PM3), it possesses a well-defined cavity of about 15 Å diameter. The cyclophyne, in turn, was obtained as a pale yellow solid, though it is air-sensitive and decomposes gradually within several days. Sankararaman, Hopf, and co-workers have also synthesized macrocyclic polyynes **90** (n = 1−7) as precursors of [4$_n$]-paracyclophynes (Chart 27).[341,342] An X-ray crystallographic analysis reveals that the trimer **91** (n = 2) possesses an expected belt-shaped structure.[341] The results of aromatization of these precursors have not been reported thus far, probably due to their high reactivity.

Chart 27

90 (n = 1~7)

91
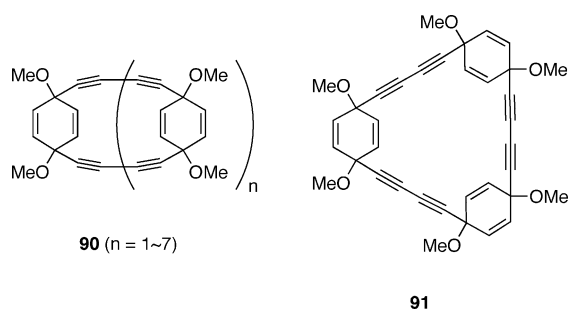
4.4. Carbon Nanorings

4.4.1. Theoretical Study of CPPAs

The [n]CPPAs possessing 1,4-phenylene and ethynylene units alternately adopt rigid and belt-shaped structures with well-defined cavities. Semiempirical calculations (AM1)

Chart 28

92: n = −1
93: n = 0
94: n = 1

95: n = 2
96: n = 3
97: n = 4

98
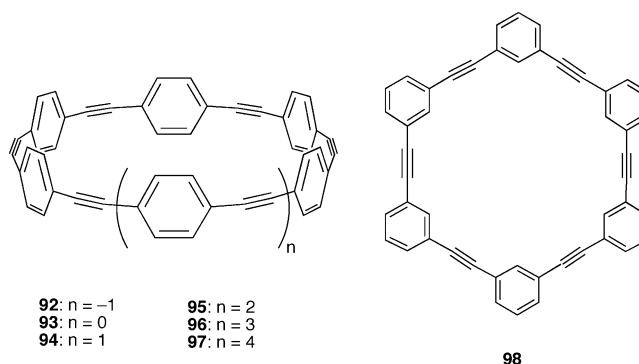
predict that CPPAs **92**−**97** (Chart 28) composed of four to nine phenylene−ethynylene units have cylindrical structures. Particularly, the cavity size in **94** is almost comparable to that of the (10.10)carbon nanotube, and it appears to be suitable for the inclusion of C$_{60}$ (0.7 nm in diameter). The bond angles of the acetylenic carbon and the strain energies are listed in Table 4. The strain energies "$E_{S[n]}$" are evaluated from eq 1, where "$E_{HF[n]}$" represents the heats of formation

$$E_{S[n]} = E_{HF[n]} - E_{HF[6]} \cdot n/6 \qquad (1)$$

of the corresponding n-ynes. Because cyclic [6]metaphenyleneacetylene ([6]CMPA; **98**) has no strain in the framework, the "$E_{HF[6]}$" value of **98** is used as a standard.

The high symmetry in the structure seems to disperse the strain energy over the molecule; the deformation of each carbon atom is small for the tortured structure. They would exist as a substance stable enough to be isolable. The predicted bond angle of [4]CPPA (**92**), which has the most strained triple bonds of the presented CPPAs, is about

Table 4. Cavity Sizes (nm), Bond Angles of Acetylenic Bonds (deg), and Estimated Strain Energies (kcal mol^{-1}) of 92−98 Based on AM1 Calculations

compd	diameter^a	bond angle^b	$E_{HF}{}^c$	$E_{HF[98]} \cdot n/6^c$	$E_{S[n]}{}^c$
92	0.86	161.7	376	304	72
93	1.07	165.4	437	380	57
94	1.31	167.8	503	456	47
95	1.52	169.5	572	532	40
96	1.74	170.8	643	609	34
97	1.96	171.6	713	684	29
98		180	456	456	0

^{a} nm. ^{b} deg. ^{c} kcal mol^{-1}.

Chart 29

99a R = H
99b R = COOn-Bu

100
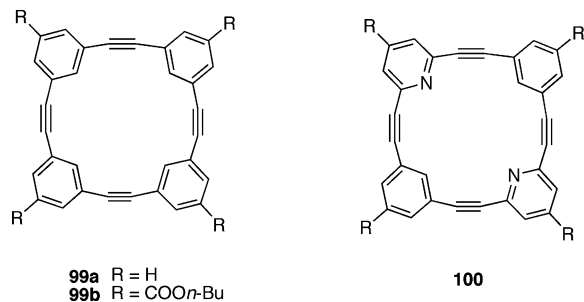
4° larger than that of stable dibenzocyclooctadiyne **81** (155.9°).[343,344]

4.4.2. Synthesis of Carbon Nanorings

In the past decade, phenylacetylene macrocycles (PAMs) have been renewedly and extensively studied from both the physicochemical and supramolecular chemical points of view.[255,332,333,345−358] Moore's and other's groups have prepared a number of PAMs with various frameworks from the corresponding phenylacetylene sequences via mainly intra- or intermolecular Sonogashira couplings.[359] The method has provided numerous fruitful results involving the synthesis of a series of cyclic [n]meta-phenyleneacetylenes, [n]CMPAs ($n = 5-7$); however, the method failed to construct [4]-CMPA (**99b**; Chart 29), probably due to the molecular strain (Scheme 9).[360] This limitation has consequently restricted the number of PAMs that are producible. (Yamaguchi, Yoshida, and co-workers later reported the successful synthesis of [4]CMPA derivatives involving two pyridine rings (**100**) via the Sonogashira reaction as a key step.[361,362])

Bromination−dehydrobromination of the corresponding cycloalkenes has been known as one of the most valuable methods for the synthesis of strained cycloalkynes. For example, the procedure can convert dibenzocyclooctadiene into dibenzocyclooctadiyne (**81**) (Scheme 10).[363−367] Thus, the procedure with good simplicity and efficiency would be applicable to the preparation of the strained CPPAs.
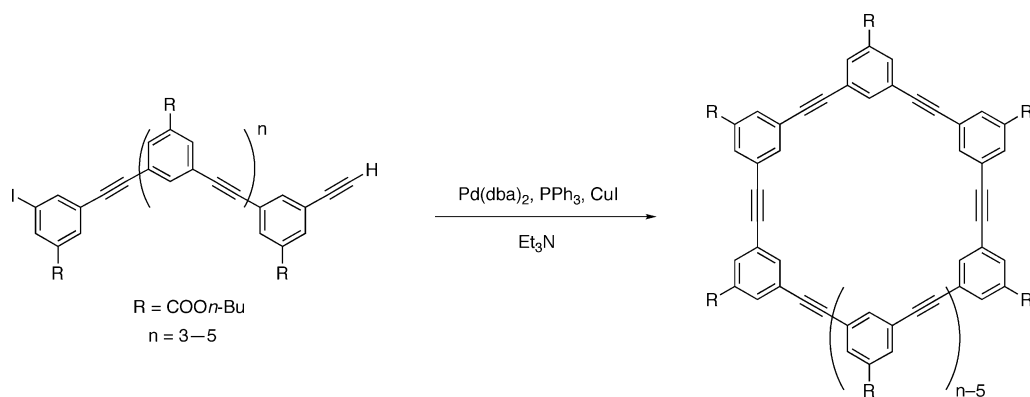
Scheme 10

81
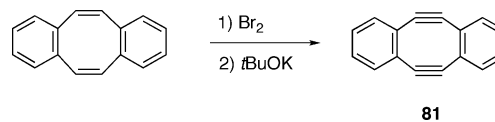
In 1996, we reported the synthesis of [6]- and [8]CPPA (**94** and **96**).[368] The report was published in the same issue in which appeared the "picotube" **75**. The precursors, the corresponding hexaenes **101**[369−372] and octaenes **102**,[373] were prepared by the McMurry coupling of 4,4′-diformylstilbene as a key step.[374−377] Subsequent treatment of the precursors with bromine in chloroform and tBuOK in diethyl ether afforded the CPPAs **94** and **96** (ca. 4:1) in 85% yield, respectively (Scheme 11).[368,378] Moreover, the syntheses of [7]CPPA (**95**) and [9]CPPA (**97**), and the related compounds **103** and **104** (Chart 30) bearing two 1,4- and 2,6-naphthylene units, were also accomplished by using a similar approach (Scheme 12).[378,379] The carbon nanorings **103** and **104** are constitution isomers of **95**. The cavity size of **104** (ca. 14.1 Å) is in the middle of those of **94** (**103**) and **95**. Moreover, cyclic [6](1,4)naphthyleneacetylene (CNA; **105**), possessing the deepest cavity in the known carbon nanorings, was also synthesized.[380] The carbon nanorings **94**−**97** and **103**−**105** were obtained as fine yellow to orange needles. When exposed to air, these crystals rapidly decomposed even at room temperature, producing a brown polymeric material. But these compounds are stable enough to be stored in a dilute solution under 0 °C for over a month. Notably, they are fairly soluble in common organic solvents except n-hexane, whereas the corresponding acyclic oligomers (para-phenyleneethynylenes) were poorly soluble at the stage of tetramer. On the other hand, the analogous synthesis of [4]CPPA (**92**) from the corresponding tetraene **106**[377,381] was unsuccessful, affording a mixture of tert-butyl alcohol adducts **107** in 30−40% yield (Scheme 13).[368] Thus, **92** seems too strained to be formed by this approach.

4.4.3. Application to the Synthesis of CMPAs

The procedure involving bromination−dehydrobromination would be widely applicable to the synthesis of strained

Scheme 9

R = COOn-Bu
n = 3−5

Pd(dba)$_2$, PPh$_3$, CuI

Et$_3$N

[n]CMPA: n = 5~7

Scheme 11

101: m = 3
102: m = 5

Chart 30

103

104

105
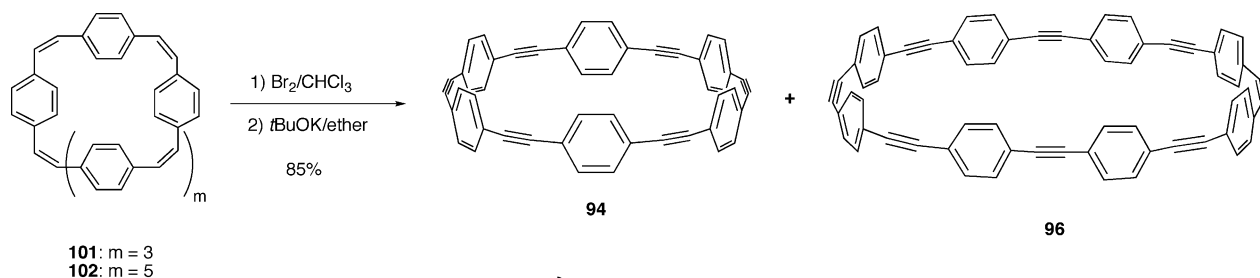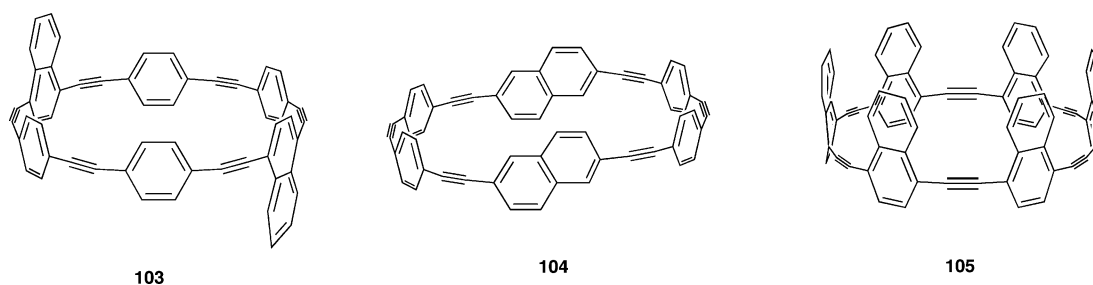
Scheme 12

Scheme 13

106

107
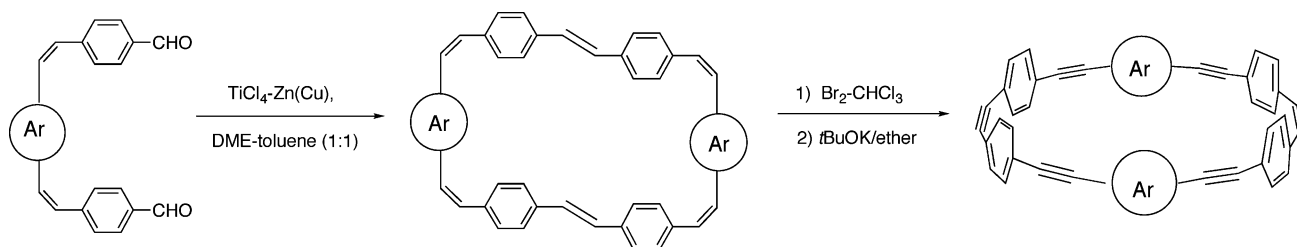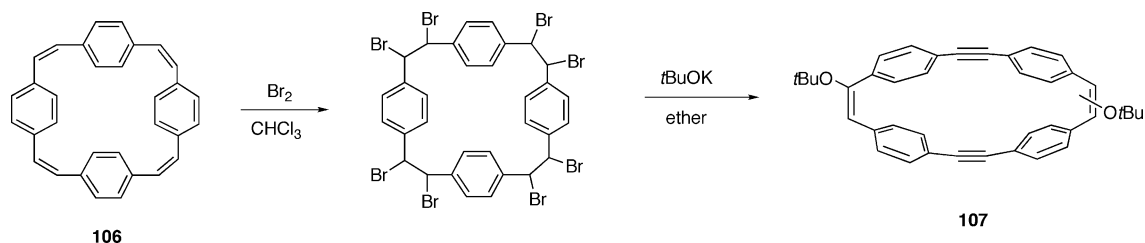
PMAs. We have prepared [4]CMPA (**99a**),[382] [3]CMPA (**109**),[383] the smallest member of this class, and their derivatives bearing methoxy groups inside the cavity, MeO-[4]CMPA (**110**)[384] and MeO[6]CMPA (**111**).[385] The MeO–CPPAs **110** and **111** bind to a C_{60} molecule in benzene solutions, although the K_a values are not very high (ca. 100 $dm^{-3} mol^{-1}$), while hydrocarbon **99c** shows little affinity for binding with fullerenes (Chart 31).[386]

4.4.4. Spectral Data of CPPAs

The selected spectral data of **94**−**97** together with those of acyclic oligomer **112** are shown in Table 5.[380] The averaged values of the inner phenyleneacetylene part of **112** (Chart 32) are shown as a reference for comparison. While the aromatic protons move slightly upfield, the sp carbons move appreciably downfield as the ring size becomes smaller (the molecular strain becomes larger). Thus, the ^{1}H NMR spectra exhibit no alternate change associated with a peripheral conjugation. Similar to the case of acyclic oligomers, no significant bathochromic shift of the longest absorptions is observed for CPPAs. On the other hand, the

emission spectra exhibit broadening and a bathochromic shift with a decrease of ring size, probably due to the increase of strain and rigidity of the molecules.

5. Complexing Abilities of Carbon Nanorings

5.1. Inclusion Complexes of Carbon Nanorings

Figure 11 shows the crystal structures of inclusion complexes of **94** with hexamethylbenzene (HMB) and **96** with four toluene molecules.[387] These are the first all-hydrocarbon inclusion complexes of cylindrical, conjugated systems. The crystals of **94·HMB** are fairly stable in air at room temperature. On the other hand, the crystal of **96·** (toluene)$_4$ tends to effloresce with loss of the toluene molecule around room temperature. The included toluene molecules in the complex **96·**(toluene)$_4$ seem to be in some attractive interaction with the inner surface of host molecules through the multiple edge-to-face interactions. The guest molecule is placed in the center of the sizable cavity of **94** by the multiple CH−π interactions.[388−392] These experimental results suggest that the concave side of the CPPAs would

Chart 31

109

R = H or tBu

110

111
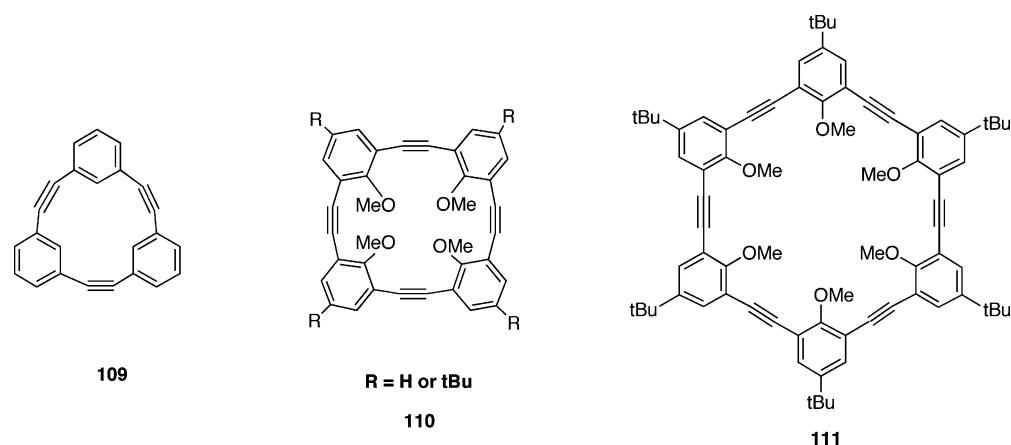
Table 5. Selected Spectral Data of 94−97 and Acyclic Oligomer 112

	94	95	96	97	112
^{1}H NMR^a	7.35	7.36	7.40	7.43	7.52^d
^{13}C NMR^a (sp carbon)	97.65	96.14	94.95	94.21	90.7^d
absorption max (log ϵ)^b	349 (5.40)	355 (5.41)	355 (5.47)	354 (5.51)	358 (5.05)
emission max^{b,c}	471	418, 448	416, 447	414, 442	398, 418

^{a} δ ppm, in CDCl$_3$. ^{b} In cyclohexane. ^{c} $\lambda_{\text{excitation}}$ = 363 nm. ^{d} Averaged values of the inner phenyleneacetylene units of the molecule.
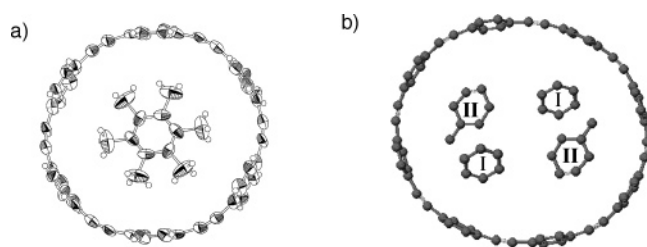
Figure 11. Molecular structures of (a) **94**·HMB and (b) **98**·(toluene)$_4$. The protons as well as the disordered methyl carbon atoms of toluene molecules **I** in the **98**·(toluene)$_4$ complex have been removed for clarity. **I** and **II** indicate toluene molecules with different spacial geometries.

Chart 32

112 (n =5)
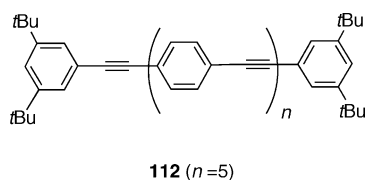
be electrostatically negative, at least comparable to the π face of benzene.

5.2. Complexation of Carbon Nanorings with Fullerenes

The carbon nanorings **94** and **103−105** form stable inclusion complexes with fullerenes in solution as well as in the solid state. The association constants (K_a) of **94**·C$_{60}$ and **94**·C$_{70}$ complexes are determined by using electronic spectra to be $(1.6 \pm 0.3) \times 10^4$ and $(1.8 \pm 0.2) \times 10^4$ dm^{-3} mol^{-1} (in benzene), respectively.[393] The spectral changes on the titration experiments are disclosed in Figure 12. Analogous to those of the calixarene complexes, in general, the spectral changes on the complexation are considerably small. On the other hand, the K_a values for the fullerene complexes of **103−105** in benzene are too large ($>5 \times 10^4$ dm^{-3} mol^{-1}) to be determined precisely.[379] Then, the K_{SV} values[143,144] (see section 2.3) are employed as a reliable measure for evaluating
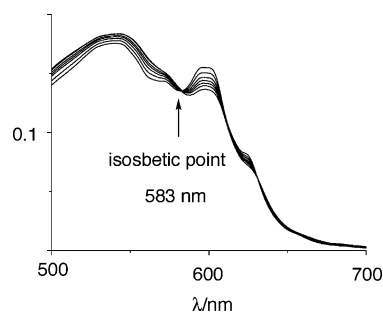
Figure 12. Absorbance spectra of mixtures of C$_{60}$ (2.0×0^{-4} mol dm^{-3}) and **96** ($0.63 \sim 6.3 \times 10^{-4}$ mol dm^{-3}).

Table 6. Diameters (Φ) of the Cavities of Hosts and K_a, K_{SV}, and $\Delta G^{\ddagger}$ Values of the Complexes

complex	Φ^a	K_a ($\times 10^{-4}$)^b	K_{SV} ($\times 10^{-4}$)^b	$\Delta G^{\ddagger}$ (CD$_2$Cl$_2$)
94·C$_{60}$	1.31	1.6 ± 0.2	7.0	9.9 ± 0.2
94·C$_{70}$		1.8 ± 0.2	14	9.6 ± 0.2
103·C$_{60}$	1.31	2.5−6.0	27	10.8 ± 0.3
103·C$_{70}$		c	26	10.1 ± 0.2
104·C$_{60}$	1.41	~10	26	<9
104·C$_{70}$		~100	430	11.9 ± 0.8
105·C$_{60}$	1.31	c	770	14.1 ± 0.3
105·C$_{70}$		c	1000	13.3 ± 0.3
95·C$_{60}$	1.53		5.6	<9
95·C$_{70}$			21	<9

^{a} nm, evaluated by AM1 calculations. ^{b} dm^3 mol^{-1}, in C$_6$H$_6$. ^{c} Undeterminable.

the stability of the complexes (Table 2). The results clearly indicate that the stability of complexes correlates well with the van der Waals contact between the host and guest (Table 6). In particular, **105**, showing the largest K_{SV} values, thus, can act as the best fluorescence sensor for fullerenes among all the known hosts. Moreover, the significantly larger K_{SV} values of **104**·C$_{70}$ than that of **104**·C$_{60}$ suggest the highly selective complexation with C$_{70}$; in fact, a solid-to-liquid extraction experiment proved the considerably high selectivity of **104** for C$_{70}$ against C$_{60}$ ($>$10:1). These findings will open the way to create tailor-made hosts for separation of higher fullerenes.

Figure 13. Molecular structure of **113·94**.

Table 7. $\Delta G^{\ddagger}$ Values of Complexes with 94[a]

guest	$\Delta G^{\ddagger}$	guest	$\Delta G^{\ddagger}$
C_{60}	9.9 ± 0.2	**118**	9.3 ± 0.3
113	9.4 ± 0.2	**114**	8.8 ± 0.2
116	9.2 ± 0.2	**115**	8.5 ± 0.2
117	9.3 ± 0.3		

[a] These values were calculated from the observed coalescence temperatures and $\Delta\delta$ values of signals of **94** (kcal·mol^{-1}).

Analogous to the case of the porphyrin dimer as mentioned in section 2.3.2, the variable-temperature NMR experiment reveals the activation of free energy ($\Delta G^{\ddagger}$) for dissociation of the fullerene complexes with carbon nanorings. Table 6 also shows a good correlation between the $\Delta G^{\ddagger}$ values and the van der Waals contact. Thus, the stability of the complexes is comparable to those of the porphyrin dimers, though the carbon nanorings are composed of only carbon and hydrogen atoms.

The molecular structure of the complex of **94** and methanofullerene derivative **113**[394−397] is shown in Figure 13.[393] The C_{60} cage of **113** is situated at a floating position in the center of the cavity of **94**, which takes a bowl-shaped conformation. The average distance between the host and guest is roughly estimated to be 3.4 Å, which is almost equal to the interlayer distance of multiwall carbon nanotubes. It is noteworthy that all the benzene rings of **94** lie over the 5:6 ring fusions of the C_{60} cage. As mentioned above, these 5:6 ring fusions represent centers of positive charge on the C_{60} surface.

In contrast to I_h-symmetrical C_{60}, fullerene derivatives are perturbed structurally and electronically. It has been known that the electronic properties of C_{60} derivatives are correlated well with the electronegativity of the attached atoms.[398] For example, the attachment of an electron-positive silicon atom considerably increases the electron density of the π systems of C_{60} derivatives **114**[399] and **115**.[400] To explore the nature of the concave surface of curved conjugated systems, the dynamic behaviors of the complexes of **94** with several fullerene derivatives **114−118** were examined (Chart 33).[401]
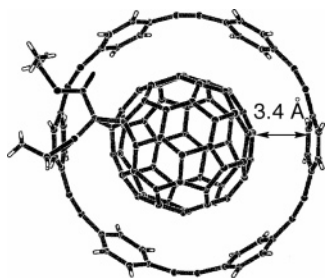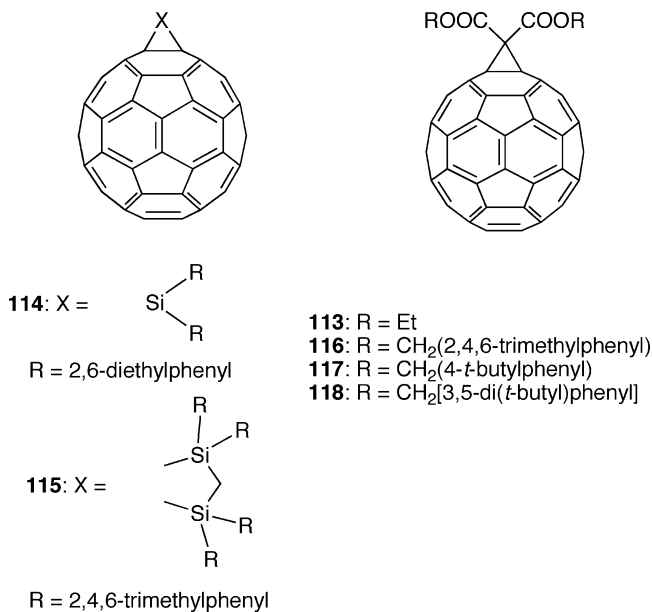
Chart 33

114: X = Si(R)(R), R = 2,6-diethylphenyl

115: X = Si(R)(R)Si(R)(R), R = 2,4,6-trimethylphenyl

113: R = Et
116: R = CH$_2$(2,4,6-trimethylphenyl)
117: R = CH$_2$(4-t-butylphenyl)
118: R = CH$_2$[3,5-di(t-butyl)phenyl]

The analyses of the NMR spectra provide $\Delta G^{\ddagger}_{dis}$ values for **94** and **113−118** (Table 7). The $\Delta G^{\ddagger}_{dis}$ values are in the order C_{60} > **113**, **116−118** > **114** > **115**. The bulkiness of the substituents has little effect on the complexation, because the $\Delta G^{\ddagger}_{dis}$ values of **113** and **116−118** are almost identical to each other. The results also suggest that the dissociation of the host and guest should occur from the side opposite to the attached group of the fullerene derivatives. The silylated fullerenes, **114** and **115**, exhibit considerably small values, with the order of the $\Delta G^{\ddagger}_{dis}$ values corresponding to the electronic properties of fullerene π systems. Therefore, an electronic repulsion between **94** and **114** (or **115**) may play an important role for weak binding between the host and guest.

5.3. Onion-Type Complexation of Carbon Nanorings

The construction of the multi-inclusion structure, reminiscent of Russian Matrioshka dolls, is one of the fascinating subjects in supramolecular chemistry.[402−411] However, no double-inclusion complexes composed of three synthetic molecules have been realized. Notably, the carbon nanorings **97** and **94** form the onion-type supramolecular structures with a C_{60} molecule in nonpolar organic solvents.[412] The structures represent a minimalistic model of multiwalled carbon nanotubes and peapods. The K_a values of **97·94** and **97·(94·C_{60})** at −60 °C were determined to be 340 ± 45 and 410 ± 80 dm^3 mol^{-1}. The values are almost identical to each other. The insensitivity suggests that the complexation with a fullerene molecule affords little electronic and structural perturbation to the host **94**. The NMR spectrum of a mixture of [6]-, [7]-, and [8]CPPAs (**94−96**) exhibits little spectral changes from their original ones, indicating the importance of complementarity to the complexation.

A tribenzo[9]CPPA derivative (**119**) was also prepared as a mixture with **103** (Chart 34), and it forms an inclusion complex with **103** in chloroform solution.[412] The titration experiments of **119** and **103** monitored by the NMR spectra determined the K_a values at various temperatures, and the data provide the thermodynamic parameters of the complexation ($\Delta H = -4.5$ kcal mol^{-1}; $\Delta S = -2.4$ cal mol^{-1} K^{-1}).[413] The negative enthalpy and entropy values indicate that substantially attractive forces would drive the host−guest complexation.

6. Conclusion

Noncovalent interaction between carbocyclic conjugated systems can be considered on the basis of following three factors: the van der Waals (VDW) interaction, the electrostatic (ES) interaction, and the charge transfer (CT) interaction. As mentioned in section 2, the globular C_{60} is tightly solvated by aromatic solvents such as benzene, favorably forms complexes with the hosts involving electron-rich aromatic systems, exhibits CT absorption bands in aromatic

Chart 34
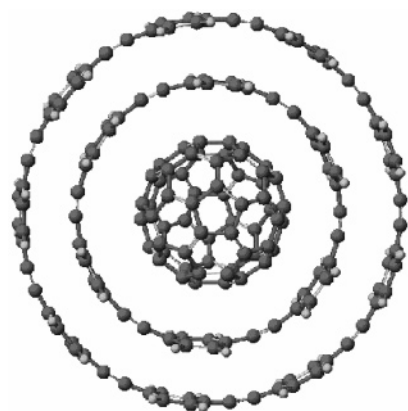
Onion-type complex **97·94·**C_{60}
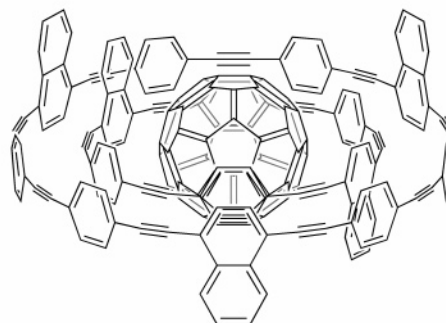
Onion-type complex **119·103·**C_{60}

solvents, and contacts with the π faces of the aromatic portions of solvents or hosts in the crystal. On the other hand, the electron affinity of C_{60} is not as strong as that of an electron acceptor, and the carbon nanorings also have relatively low electron-donating properties. In fact, the titration experiments showed only slight changes in the CT bands in Figure 12, compared with those of *N,N*-dimethylaniline in Figure 1. Moreover, the crystallographic analysis of the complex **94·**C_{60} reveals little correlation with the molecular orbital interaction between the HOMO of **94** and the LUMO of methanofullerene **113**. These results indicate that the CT interaction would be negligible in the complexation. Although the carbon nanorings presented here are composed of only carbon and hydrogen atoms, the stabilities of the complexes with fullerenes are comparable to those of the zinc porphyrin dimer **47a**−Zn. The results indicate that other attractive forces in addition to the VDW force are operative between the curved conjugated systems. Thus, the ES interaction remains the most probable driving force for the complexation.

The molecular structures of the complexes **94·**HMB and **96·**(toluene)$_4$ presented here reveal that the concave surfaces of carbon nanorings have an electrostatically negative potential. The molecular structure of the complex **94·113** also reveals that all the benzene rings of **94** lie over the 5:6 ring fusions of the C_{60} cage of **113**. These 5:6 ring fusions represent centers of positive charge on the C_{60} surface, whereas the 6:6 fusions represent centers of negative charge. These results suggest that the major driving force for the complexation would be the electrostatic interaction between the electrostatically opposite concave and convex surfaces of **94** and **113**.

People may consider that the novel supramolecular properties of C_{60} are due to its novel π-electron structure. However, the supramolecular properties of the convex surface of carbon nanotubes (CNs) are similar to those of fullerenes, although CNs have few 5:6 fusions in the π system. Moreover, we have discovered the onion-type complexation of carbon nanorings. No phenylacetylene macrocycles without electron-withdrawing substituents on their aromatic rings have shown aggregation in nonpolar solvents thus far, because $\pi-\pi$ stacking between planar aromatic hydrocarbons causes an electrostatically repulsive force.[414−428] The present results, thus, evidently prove the substantial difference of electronic properties between planar and curved conjugated systems. The electrostatic interaction is substantially operative between curved conjugated systems

in addition to the dispersion force. The charge distribution owing to the difference between 5:6 and 6:6 ring fusions controls the mutual orientation in the crystal packing of complexes. The attractive interactions also play an important role in the spontaneous formation of fullerene peapods and other new materials based on carbon nanotubes. Further experimental and theoretical studies on these complexes and related substances will deepen understanding of the novel nature of fullerene and other curved π-electron systems.

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