

Complexation of carbon nanorings with fullerenes*

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Abstract: To explore the supramolecular properties of the hollow space of carbon nanotubes, the belt-shaped conjugated systems with sizable and deep cavities are intriguing molecules. Recently, we found that the “carbon nanorings”, cyclic [6]paraphenyleneacetylene ([6]CPPA), and the related compounds involving two naphthylene rings, form stable inclusion complexes with fullerenes in solution as well as in the solid state. The stability of these complexes correlates well with the van der Waals (VDW) contact between the host and guest. Thus, carbon nanorings having a deep cavity should form considerably stable complexes with fullerenes. In this context, we have designed a new carbon nanoring, cyclic [6](1,4)naphthyleneacetylene. The host forms considerably stable inclusion complexes with fullerenes and can act as the best fluorescence sensor for fullerenes among all the known hosts. The NMR spectra reveal the formation of two major conformational isomers, in which five or six naphthylene rings surround a guest molecule to gain wide contact area. The high affinity between C₆₀ and naphthylene rings similar to an ion-dipolar interaction plays an important role in the novel guest-induced conformation fixation.

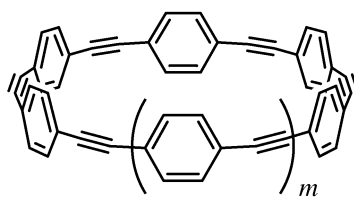
Keywords: noncovalent interactions; curved conjugated systems; fullerenes; inclusion complexes.

INTRODUCTION

Recently, various layered carbon networks having a curled and closed structure such as carbon nanotubes, bucky onions, and fullerene-peapods have attracted much attention. Although the nature of concave–convex interaction between the curved graphene sheets should be important for the formation and properties of these materials, they are yet to be well understood owing to the absence of good model compounds. In this relation, considerable efforts have been made for the synthesis of belt-shaped conjugated systems [1]. In 1996, we synthesized cyclic [6]- and [8]paraphenyleneacetylenes, **1** and **2** ([6]- and [8]CPPA) [2]. According to the theoretical calculation (AM1), these molecules have smooth belt-shaped structures like a cut piece of carbon nanotube, and then may be termed “carbon nanorings”. The high symmetry in the structure seems to disperse the strain energy over the molecule; therefore, it would exist as a substance stable enough to be isolable. In particular, the cavity size of **1** (1.32 nm) seems suitable for inclusion of C₆₀ (0.7 nm in diameter), although it is slightly too small when the depth of the p-orbitals is considered. The host–guest chemistry of carbon nanorings and fullerenes would give an insight into the concave–convex π – π interaction.

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1; $m = 1, 2; m = 3$

COMPLEXATION OF [6]CPPA WITH FULLERENES

[6]CPPA **1** forms rather weak inclusion complexes with hexamethylbenzene (HMB) [3]. The molecular structure (Fig. 1a) reveals several unique characteristics: (1) The host molecule has a slightly distorted, but nearly smooth cylindrical structure in the crystal. (2) The guest molecule is placed in the center of the sizable cavity of **1** through the multiply CH- π interactions. These experimental results suggest that the concave side of **1** would be electrostatically negative at least comparable to the π -face of benzene. The host **1** forms unusually stable complexes with C_{60} and C_{70} in solution as well as in solid [4]. Although the host molecule is composed of only carbon and hydrogen atoms, the association constants (K_a) are quite high (**1**· C_{60} for $1.6 \pm 0.3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ and **1**· C_{70} for $1.8 \pm 0.2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ in C_6H_6). The variable-temperature NMR experiments also reveal the activation of free energy (ΔG^\ddagger) for dissociation of **1**· C_{60} to be $9.9 \pm 0.3 \text{ kcal mol}^{-1}$ ($T_c = -80 \pm 5 \text{ }^\circ\text{C}$) in CD_2Cl_2 . Although attempted X-ray analysis of **1**· C_{60} have failed so far, good single crystals of the complex of **1** with bis(ethoxycarbonyl)methanofullerene (**3**) were obtained from a toluene solution. The molecular structure obtained (Fig. 1b) reveals that the C_{60} cage of **3** is not deeply embedded in the cavity, but situated at a floating position from the center of cavity of **1**, which takes a bowl-shaped conformation. Even in this ball-on-a-bowl structure, all the benzene rings of **1** face near the C_{60} cage of **3**. We have concluded from the results that the concave-convex π - π interaction plays an important role in the complexation, and the cavity size of **1** is slightly smaller than the size of C_{60} as expected. These findings promoted us to investigate the structural tuning of the host molecules.

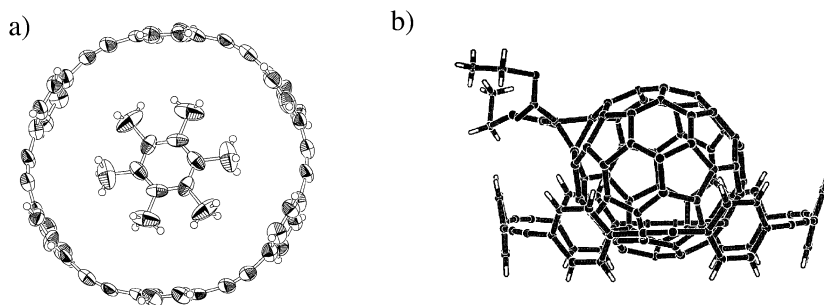
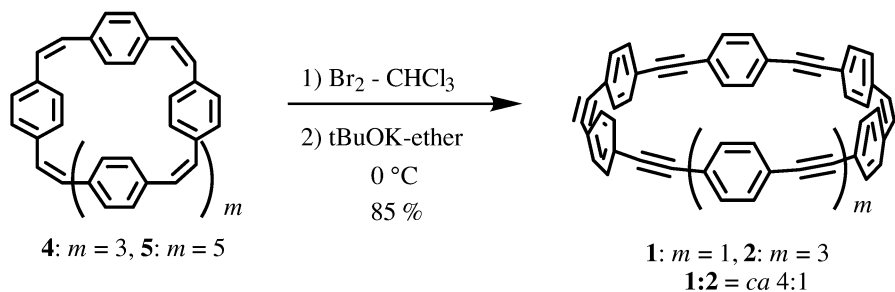


Fig. 1 Molecular structure of (a) **1**·HMB and (b) **1**·**3**.

IMPROVED SYNTHESIS OF CPPAs

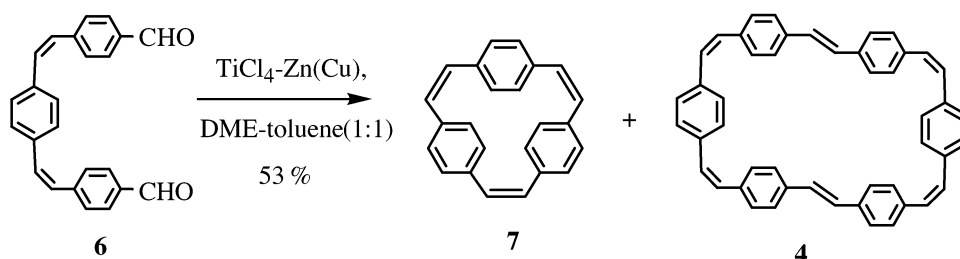
To understand the supramolecular properties of curved conjugated systems more deeply, the development of practical syntheses of CPPAs has become an important problem of the study. We prepared **1** and **2** from the corresponding cyclophanepolyenes **4** and **5**, which are usually a mixture of geometric isomers, though bromination-dehydrobromination in good yields (Scheme 1) [2]. However, the avail-

ability of the precursors has been unsatisfactory, because the synthesis of them using the Wittig or McMurry reaction suffered from low yields and difficulty in purification [5]. Therefore, improvement of the synthesis was desired.



Scheme 1 Synthesis of **1** and **2**.

The McMurry reaction of 1,4-bis(4-formyl-(*Z*-styryl)benzene (**6**) in tetrahydrofuran (THF) afforded (*Z*³)-[2.2.2]paracyclophanetriene (**7**) in 50 % yield [6]. The paper did not describe the yield of **4** as a dimer. In order to improve the yield of **4**, we investigated the reaction under several conditions (Scheme 2), and found that the use of a mixed solvent of toluene/DME (1:1) resulted in the formation of **4** in 53 % yields. Notably, the known isomer (*Z,Z,E*)²-**4** was formed predominantly [7]. The high *E*-selective double-bond formation would play a key role for the cycloligomerization. Variation of the ratio between toluene and DME (2:1 to 1:9) resulted in little change of the yields, and the reaction in only DME or THF/toluene (1:1) gave **7** as a major product together with **4**. The strong solvent effects suggest that the reactive intermediate generated in DME/toluene would be different from those generated in solvents without toluene. Although the elucidation of the reactive intermediate has been unsatisfactory, the modified reaction would be promising for the preparation of macrocyclic compounds of physicochemical interest.



Scheme 2 Improved synthesis of **4**.

PHYSICAL PROPERTIES OF CPPAs

We have also prepared [7]- and [9]CPPA (**8** and **9**) by using the modified McMurry coupling as a key step [7]. According to the theoretical calculation, these carbon nanorings composed of six to nine phenyleneacetylene units have a cylindrical structure, whose cavity sizes are 1.31, 1.53, 1.74, and 1.96 nm, respectively. Their selected spectral data together with those of an acyclic oligomer **10** are shown in Table 1. The averaged values of the inner phenyleneacetylene part of **10** are taken as reference for comparison. While the aromatic protons move slightly up-field, the sp carbons move appreciably down-field as the ring-size becomes smaller (the molecular strain becomes larger). Thus, the ¹H NMR spec-

tra exhibit no alternate change associated with a peripheral conjugation. The absorption and emission spectra of CPPAs and **10** are shown in Fig. 2. Similar to the case of acyclic oligomers [8], no significant bathochromic shift of the longest absorptions are observed for CPPAs. On the other hand, the emission spectra exhibit broadening and bathochromic shift with decrease of ring size, probably due to the increase of strain and rigidity of the molecules.

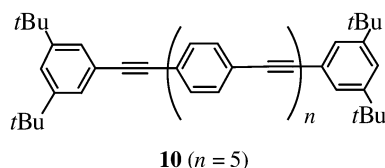


Table 1 Selected spectral data of CPPAs and an acyclic oligomer **10**.

	1	8	2	9	10
$^1\text{H NMR}^{\text{a}}$	7.35	7.36	7.40	7.43	7.52 ^d
$^{13}\text{C NMR}^{\text{a}}$ sp carbon	97.65	96.14	94.95	94.21	90.7 ^d
Absorption max. ($\log \epsilon$) ^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 .

^bIn cyclohexane.

^c $\lambda_{\text{excitation}} = 363 \text{ nm}$.

^dAveraged values of inner phenyleneacetylene units

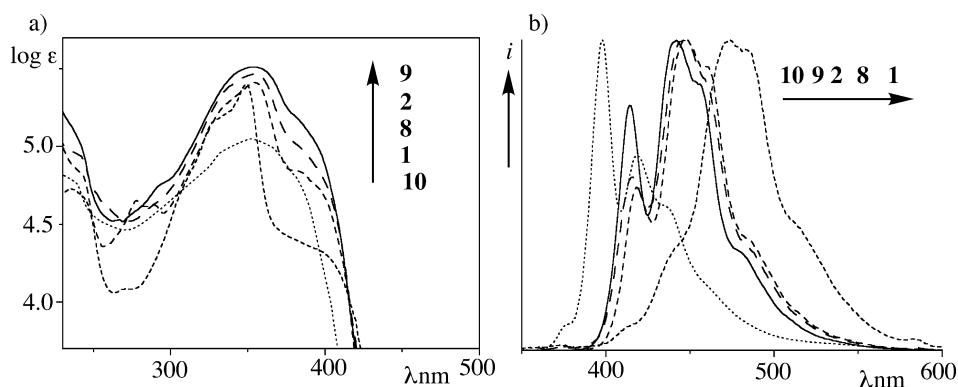
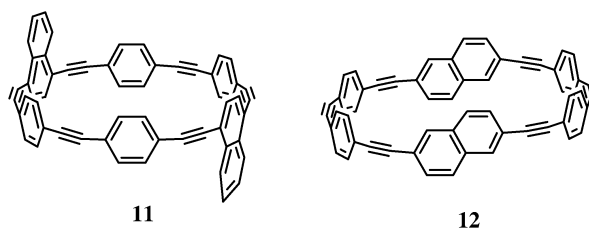


Fig. 2 (a) Absorption and (b) normalized emission spectra of CPPAs and **10** in cyclohexane.

COMPLEXATION WITH CARBON NANORING WITH VARIOUS CAVITY SIZES

We also designed new carbon nanorings **11** and **12** having 1,4- and 2,6-naphthylene rings, constitution isomers of [7]CPPA **8**. The cavity size of **12** (ca. 14.1 Å) is in the middle of **11** and **8**. The synthesis is accomplished by employing the modified McMurry reaction [9].



The stability of fullerene complexes is generally evaluated in terms of the association constant (K_a) determined by means of absorption spectra. However, we have found that the K_a values for the fullerene complexes of **11** and **12** in benzene are too large ($>5 \times 10^4$) to be determined precisely [10], and the Stern–Volmer constants (K_{SV}) determined by means of fluorescence spectra would provide a reliable measure for evaluating the stability of the complexes; the presence of a fullerene quenches the intense fluorescence emission of carbon nanorings very effectively. The K_{SV} values are listed in Table 2. The results clearly indicate that the stability of complexes correlates well with the van der Waals (VDW) contact between the host and guest. Moreover, the significantly larger K_{SV} values of **12**· C_{70} than that of **12**· C_{60} suggests the highly selective complexation with C_{70} ; in fact, upon competitive complexation by **12** through solid-to-liquid extraction from a fullerite (C_{60} : C_{70} = ca. 1:1) in CD_2Cl_2 , the NMR spectrum of the extract was almost identical to that of **12**· C_{70} , indicating the considerably high selectivity ($>10:1$) for C_{70} against C_{60} . These findings will also open the way to create tailor-made hosts for separation of higher fullerenes.

Table 2 Diameters (Φ)^a of the cavity of hosts and K_{SV} values^b of the complexes.

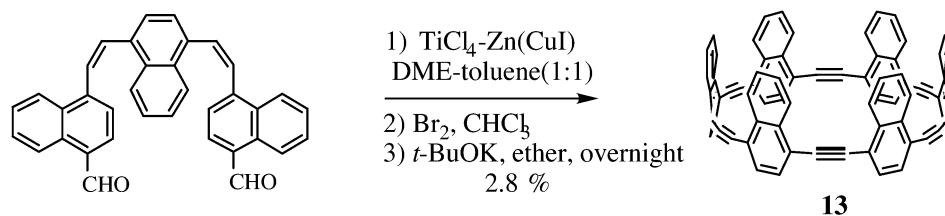
	1	11	12	8	2
Φ	1.31	1.31	1.41	1.53	1.74
K_{SV} C_{60}	7.0×10^4	2.7×10^5	2.6×10^5	5.6×10^4	$<10^4$
K_{SV} C_{70}	1.4×10^5	2.6×10^5	4.3×10^6	2.1×10^5	$<10^4$
K_{C70}/K_{C60}	2.0	1.0	16.5	3.7	

^anm, evaluated by AM1 calculations.

^bdm³ mol⁻¹, in C_6H_6 .

CYCLIC [6]NAPHTHYLENEACETYLENE

Carbon nanorings having a deep cavity should make very stable complexes with fullerenes. In this context, we designed a new carbon nanoring, cyclic [6](1,4)naphthyleneacetylene **13**. According to theoretical calculations, the cavity size of **13** is identical to that of **1**, but the cavity is deeper than that of **1**. However, the cavity of **13** is not preorganized, because **13** has eight rotational isomers, and these isomers possess almost the same formation energies owing to little steric congestion between adjacent naphthylene units. Therefore, **13** should exist in an equilibrium mixture of the rotational isomers with statistical distribution [11]. Synthesis of **13** was accomplished by the similar synthetic method of **1** (Scheme 3) [12,13]. The compound is sensitive to acid and oxygen, but solid **13** was stable enough to be stored in a refrigerator over a day, whereas that of **1** rapidly decomposed even at 0 °C under air. The NMR spectrum of **13** at 30 °C reveals high symmetry of the molecules, and these signals are almost unchanged even at -90 °C (in CD_2Cl_2), clearly indicating that each aromatic ring rotates faster than the NMR time scale in the measurable temperature range.



Scheme 3 Synthesis of **13**.

The titration experiments using emission spectra determined the K_{SV} values of the fullerene complexes (**13**· C_{60} for $1.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1}$ and **13**· C_{70} for $7.7 \times 10^6 \text{ dm}^3 \text{ mol}^{-1}$ in C_6H_6). As expected, the values are considerably large; the value for **13**· C_{60} is ca. 40 times larger than those of **11**· C_{60} in accordance with the increase of contact area. It is noteworthy that **13** can act as the best fluorescence sensor for fullerenes among all the known hosts [14]. The value for **13**· C_{60} is larger than that for **13**· C_{70} in contrast to the other complexes. According to the molecular model construction, the contact areas between the host and guest seem to be the same. The difference of K_{SV} values would be attributed to the electronic properties of C_{60} and C_{70} . The relatively flat midsection of C_{70} exhibits the lower affinity to the aromatic π -surfaces than the surface of C_{60} , because of the relatively high electron density.

The analyses of ^1H and ^{13}C NMR spectra afford important information concerning the supramolecular dynamics of these complexes. Figures 3a and 3b shows the spectral change of **13**· ^{13}C -rich C_{60} . These signal changes indicate the presence of two independent dynamic processes in the complexation: dissociation of the complex [$\Delta G^\ddagger = 14.1 \pm 0.3 \text{ kcal mol}^{-1}$ at 10°C ; $\Delta H^\ddagger = 16.7 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 12.1 \text{ cal mol}^{-1} \text{ K}^{-1}$] and interconversion among rotational isomers [$\Delta G^\ddagger = 11.7 \pm 0.7 \text{ kcal mol}^{-1}$ at -47°C ; $\Delta H^\ddagger = 13.0 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 5.8 \text{ cal mol}^{-1} \text{ K}^{-1}$]. The ΔG^\ddagger value for dissociation is considerably larger than those of **1**· C_{60} ($9.9 \pm 0.2 \text{ kcal mol}^{-1}$) and **11**· C_{60} ($10.8 \pm 0.3 \text{ kcal mol}^{-1}$) in accordance with the high stability of the complex. It is noteworthy that the flipping of the naphthylene rings must occur without dissociation of the complex. It is reasonable that the ΔS^\ddagger value of the flipping is smaller than that of the dissociation involving solvation and desolvation processes. Figure 3a also reveals that the flipping motion becomes slow enough for NMR time scale at the temperature, and that the complex **13**· C_{60} exists in an equilibrium mixture of two major and some minor isomers. The chemical shifts of major isomers of **13**· C_{60} (139.94 and 139.84 ppm) are considerably higher than those of the other complexes (**1**· C_{60} for 140.98 ppm; *anti*-isomer of **11**· C_{60} for 140.68 and *syn*-isomer for 140.59 ppm), which would correspond to the number of the faced naphthylene rings.

Figures 3c and 3d shows the ^1H NMR spectra of **13** and C_{60} with 1:1 and 2.5:1 ratios in CD_2Cl_2 at -90°C . These spectra exhibit the presence of a highly symmetric isomer together with relatively low symmetric isomers in the solution. The signals corresponding to the α -positions of naphthylene rings are informative to the assignment of these isomers. The signals of **13**· C_{60} split into two multiplets of 8.2~8.3 and 8.5~8.6 ppm ranges at low temperatures, and the integration of the signals at 8.5~8.6 ppm are quite small (<1:10). When the carbon nanorings accommodate a fullerene in the cavity, the protons at the near side of the fullerene resonate at the higher magnetic field than the corresponding protons of the free host, and the protons at the far side do at the lower magnetic field. Combined with these results, two major isomers of **13**· C_{60} would be assignable to u_6 - and u_5d -isomers; five or six naphthylene rings of **13** surround a fullerene molecule to gain the wide contact area (Scheme 4). In the transition state of the flipping process, four or five naphthylene rings should be attached to the slightly floating guest molecule not to escape from the cavity. The high affinity between C_{60} and naphthylene rings similar to an ion-dipolar interaction plays an important role in the novel guest-induced conformation fixation [15]. The findings may be widely applicable to the construction of supramolecular structures having machine-like characters.

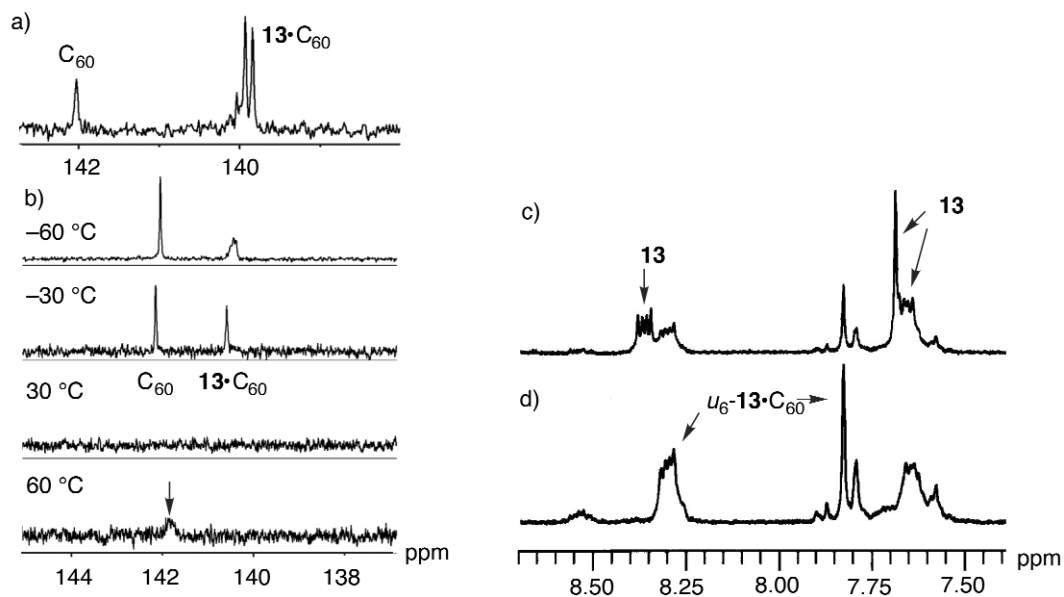
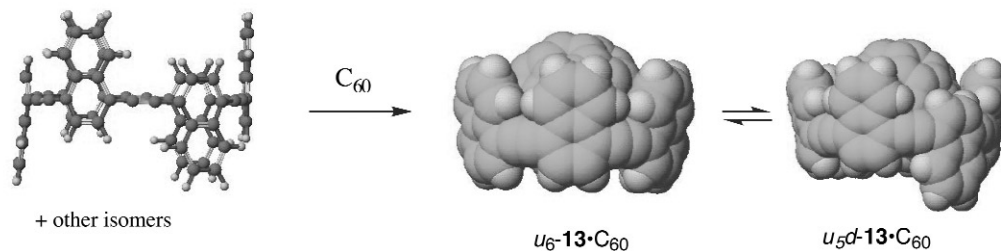


Fig. 3 VT ^{13}C NMR spectra of ^{13}C -enriched C_{60} , (a) in the presence of 0.8 equiv of **13** in CD_2Cl_2 at $-90\text{ }^\circ\text{C}$; (b) in the presence of 0.4 equiv of **13** in CDCl_3 at -60 , -30 , 30 , and $60\text{ }^\circ\text{C}$; (c) Portion of ^1H NMR spectra of **13** at $-90\text{ }^\circ\text{C}$ in CD_2Cl_2 in the presence of 0.4 equiv of C_{60} ; (d) in the presence of an equiv of C_{60} .



Scheme 4 Conformational change on complexation of **13** with C_{60} .

CONCLUSION

Noncovalent interaction between carbocyclic conjugated systems can be considered on the basis of following three factors, the VDW interaction, the electrostatic (ES) interaction, and the charge-transfer (CT) interaction. The weak CT interaction has been thought as a main driving force of the fullerene complexes so far [16]. However, the recent theoretical and experimental studies have revealed that CT energy is much smaller than ES and VDW energies in noncovalent interactions [17]. Actually, the electron affinity of C_{60} is not so strong as an electron acceptor, and electron-donating properties of the carbon nanorings as a simple hydrocarbon are relatively poor. The high affinity between carbon nanorings and fullerenes is hardly explained in terms of dispersion force (VDW interaction) alone. The ES interaction remains the most probable driving force for the complexation. The supramolecular properties of fullerenes would be understandable by possessing positive electronic potential of the convex surface [18]. Recent theoretical studies have also predicted that curved aromatic hydrocarbons should be polarized in regard to the convex and concave side because of the unsymmetrical nature of their p-orbitals.

Although the results of theoretical calculations have been controversial as to the direction of polarization [19], an ES attractive force between the electrostatically opposite concave and convex surfaces as well as the dispersion force would play an important role in the formation of these complexes and hence the spontaneous formation of layered carbon nanotubes, bucky onions, and fullerene-peapods.

ACKNOWLEDGMENTS

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11. The compound **13** has eight rotational isomers: u_6 , u_5-d , u_4-d_2 , $u_3-d-u-d$, u_2-d-u_2-d , u_3-d_3 , $u_2-d-u-d_2$, and $(u-d)_3$, where u represents an up-conformation and d does a down-conformation of the 1,4-naphthylene units of **13**; the statistical distributions of these isomers are 1:6:6:6:3:3:6:1.
12. T. Kawase, M. Tsutsumi, N. Shiono, M. Oda. Unpublished work.
13. Selected physical and spectral data of **13**: orange fine needles; mp >150 °C (decomp); MS (FAB) m/z 901 ($[M+H]^+$); 1H NMR ($CDCl_3$, 270 MHz) δ = 7.62 (s, 12H), 7.60~7.63 (m, β -protons, 12H), 8.38~8.41 (m, α -protons, 12H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 99.77, 122.37, 126.48, 127.18, 129.70, 132.85; IR (KBr) ν/cm^{-1} 2159 (C=C); UV-vis (CH_2Cl_2) λ_{max}/nm (log ϵ) 403sh (5.02), 423 (5.23); Fluorescence (CH_2Cl_2) λ_{max}/nm 515, 551, 594.
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