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Inclusion of [60]Fullerene in a Self-assembled Homooxacalix[3]arene-based Dimeric Capsule Constructed by a Pd^{II}–pyridine Interaction. The Li^+-binding to the Lower Rims can Improve the Inclusion Ability

Atsushi Ikeda, Hiromi Udzu, Makoto Yoshimura and Seiji Shinkai*

Department of Chemistry & Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan

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Abstract—A capsule-like cage molecule was constructed by dimerization of pyridine-containing homooxacalix[3]aryl esters utilizing a Pd^{II}–pyridine interaction. Interestingly, it was found that this molecule can include [60]fullerene in the inner cavity and the exchange rate is slower than the ^1H and ^{13}C NMR time-scales, giving rise to new separate NMR peaks assignable to the capsule[60]fullerene complex. From the integral intensity ratio the association constant (K_{ass}) was estimated to be 39 $dm^3\ mol^{-1}$ (at 30°C). The $\Delta\delta_H$ between H_{ax} and H_{eq} in the $ArCH_2O$ methylene protons gave a sign that when Li^+ cations are bound to the ionophoric lower rims, the capsule molecule is changed to a more flattened conformation which is more suitable to [60]fullerene inclusion. This Li^+-induced preorganization enhanced the K_{ass} up to 2100 $dm^3\ mol^{-1}$(at 30°C). Thus, the present study is the first example that [60]fullerene is included in a capsule-like cage molecule and the exchange rate appears to be the slower than the NMR time-scales. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

In 1994, we[1] and Atwood et al.[2] discovered that *p-tert*-butylcalix[8]arene selectively includes [60]fullerene in carbon soot and forms the precipitate with 1:1 stoichiometry. This is a very novel and very useful purification method to obtain [60]fullerene in the large quantity and with high purity and opened a door to the new marriage of the third generations of inclusion compounds and carbon clusters.[1–3] It has been believed that the origin of selective inclusion stems from the conformity of the [60]fullerene size with the calix[8]arene cavity.[4] However, when this complex was solubilized in solution (e.g. by heating or using good solvents), it was dissociated into each component and any spectroscopic indication for the complex formation could not be found.[4] This means that this complex can stably exist only in the solid state. More recently, it was shown that certain calix[*n*]arenes and their analogues can interact with [60]fullerene even in solution.[5–13] These compounds (i.e. calix[5]arenes, calix[6]arenes, homooxacalix[3]arenes and cyclotriveratrylenes) all satisfy two prerequisites for inclusion, viz. a preorganized cone conformation and a proper inclination of the benzene rings.[4,5a,14] The X-ray structure for a [60]fullerene-calix[5]arene complex showed that [60]fullerene is included in a cavity composed of two calix[5]arene half-bowls.[8] This picture stimulated us to design such a capsule molecule useful for inclusion of [60] fullerene from two calix[*n*]arenes.[15] The survey of the precedent references taught us that a covalent bond and a hydrogen-bonding interaction have so far been utilized for the construction of calixarene-based dimeric capsule molecules.[14] Here, it occurred to us that the utilization of a coordination bond has been an escaped idea, for Fujita et al.[16] and Stang et al.[17] have shown a number of attractive examples that the coordination bond is very useful for the construction of self-assembled supramolecular structures. We thus designed compound **3**: presumably, calix[4]arenes are not suitable as a building-block to the present purpose because they cannot interact with [60]fullerene.[6] On the other hand, calix[5]arenes and calix[6]arenes do interact with [60]fullerene[5–13] but the increase in the number of the coordination sites leads to the increase in the mismatching probability to yield the undesired oligomeric aggregates. We considered, therefore, that homooxacalix[3]arenes which can also interact with [60]fullerene[6] and have only three coordination sites would be the most suitable building-block. The ^1H NMR and mass spectroscopic studies and VPO measurements showed that two homooxacalix[3]arenes (**1**) dimerize in the presence of three equivalents of Pd^{II} ($(Ph_2PCH_2CH_2CH_2PPh_2)\cdot(OTf^-)_2$) (**2**) into a molecular capsule.[18] Very interestingly, we have found that this capsule molecule can specifically include [60]fullerene (Scheme 1).

Keywords: dimeric capsule; homooxacalix[3]arene; [60]fullerene; Pd–pyridine interaction; Li^+-binding.

* Corresponding author. Tel.: +92-642-3583; fax: +92-642-3611; e-mail: seijitcm@mbox.nc.kyushu-u.ac.jp

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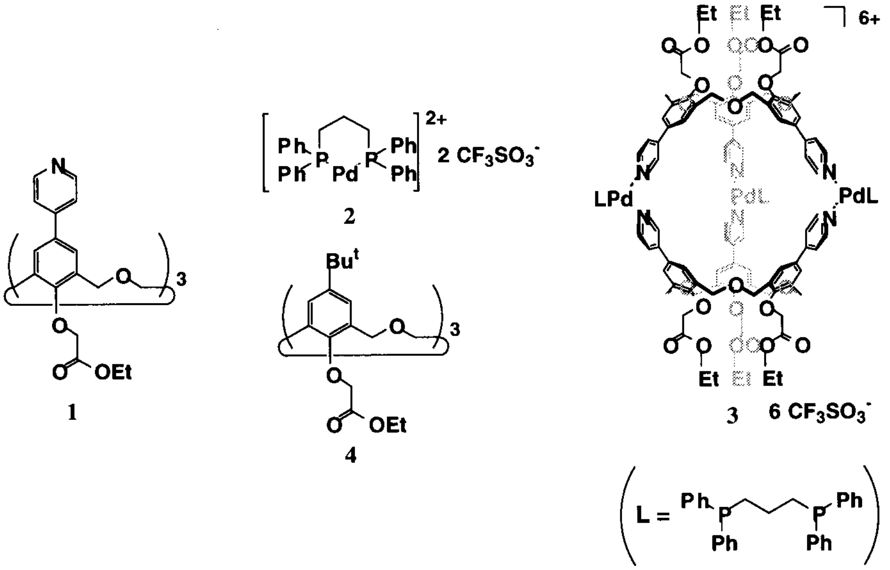


Scheme 1.

Results and Discussion

Inclusion of [60]fullerene

As shown in Fig. 1, a 2:3 **1**/**2** mixture gave a ^{1}H NMR spectrum assignable to **3** with a D_{3h}-symmetrical structure.[18] Expecting that the cavity would be able to capture large or anionic guest molecules, we estimated the inclusion ability by ^{1}H NMR spectroscopy. The guest molecules tested herein were DMF, DMSO, nitromethane, adamantane, 1,3,5-trimethylbenzene, 1,2,4,5-tetramethylbenzene, anthracene, pyrene, sodium picrate, sodium tetraphenylborate, sodium tetrakis[3,5-bis(trifluoromethyl)penyl]borate, etc. However, none of these compounds could give the separate NMR peaks or induce the significant chemical shift change attributable to the host–guest complex formation. Examination of the CPK molecular models reveals that three windows in **3** are large enough to allow permeation of these guest molecules. Very interestingly, only when ^{13}C-enriched [60]fullerene (^{13}C content ca. 12%) was added, new peaks appeared both in the ^{1}H and ^{13}C NMR spectra (Figs. 1 and 2).

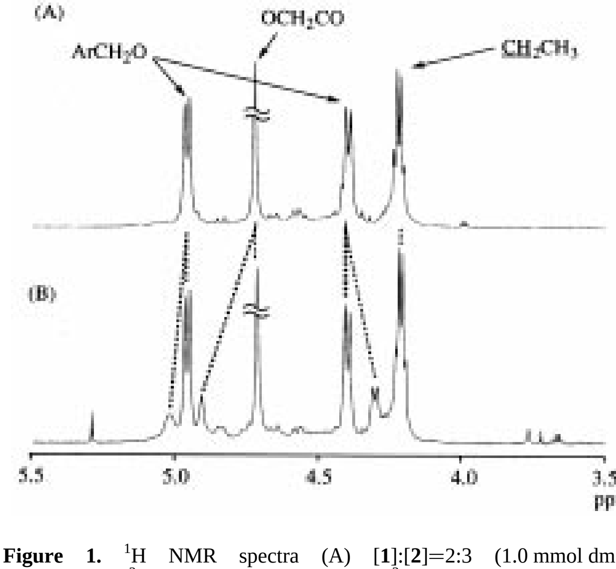


Figure 1. ^{1}H NMR spectra (A) [**1**]:[**2**]=2:3 (1.0 mmol dm^{-3}: 1.5 mmol dm^{-3}) and (B) [**3**] (0.50 mmol dm^{-3}) in the presence of [60]fullerene (5.8 mmol dm^{-3}): 600 MHz, $Cl_2CDCDCl_2$, 25°C.

In the ^{13}C NMR spectrum (Fig. 2), a new separate peak appeared at higher magnetic field (140.97 ppm) than the peak for free **3** (142.87 ppm). This peak is assignable to the **3**[60]fullerene inclusion complex and the peak separation implies that the complexation–decomplexation exchange rate is slower than the ^{13}C NMR time-scale. According to Cram's studies on molecular containers,[19] the rate of the guest liberation from a hemicarcerand is related not only to the size of the guest molecules but also to the rigidity and the shape. For example, adamantane ($C_{10}H_{16}$) which is rigid and nearly spherical is much more difficult to liberate than flexible tripropyl phosphate ($C_9H_{21}O_4P$).[19] [60]Fullerene is exactly classified into the rigid and spherical guest and therefore the exchange rate can be slower than the ^{13}C NMR time-scale. This consideration manifests that the above-mentioned guest molecules are either smaller or more flexible than [60]fullerene and therefore, cannot be efficiently included in the cavity. It is also noteworthy that the **3**·[60]fullerene complex gives a single peak (Fig. 2). This implies that included [60]fullerene still rotates in a speed faster than the ^{13}C NMR time-scale. In the presence of noncapsular **1** (instead of capsular **3**) the ^{13}C NMR spectrum was scarcely changed. The result is consistent with our previous finding that the ethoxycarbonylmethoxy derivatives of homooxacalix[3]arene cannot interact with [60]fullerene in the absence of alkali metal cations.[6] When **2** and [60]fullerene were mixed in an equimolar ratio (1.0 mmol dm^{-3}), the [60]fullerene peak shifted by 0.07 ppm to higher magnetic field. It is known that Pd^0 coordinates to [60]fullerene to form the η-complexes,[20] but to the best of our knowledge there is no evidence for the interaction between Pd^{II} and [60]fullerene.[21] The slight

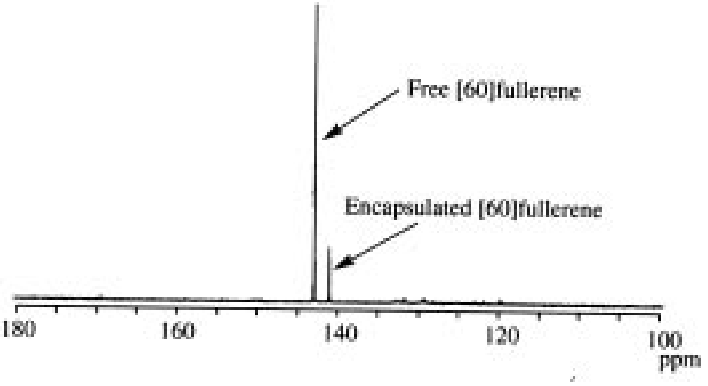


Figure 2. ^{13}C NMR spectrum of ^{13}C-enriched [60]fullerene (5.8 mmol dm^{-3}) in the presence of **3** (5.0 mmol dm^{-3}): 150 MHz, $Cl_2CDCDCl_2$, 25°C.

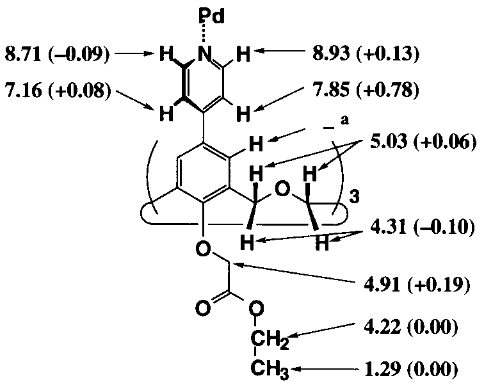
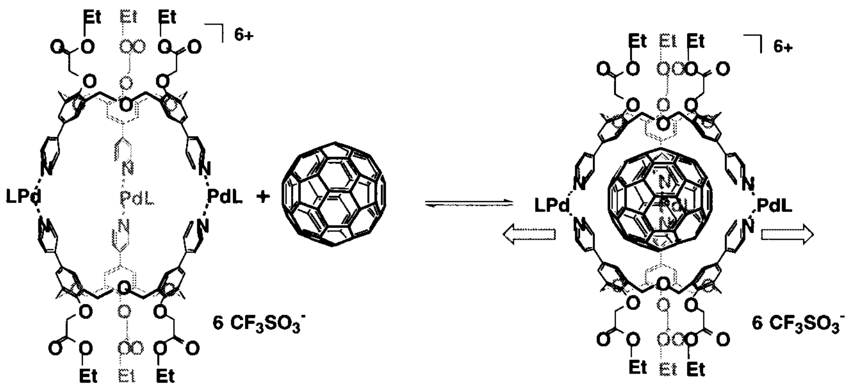


Figure 3. Assignment of the **3** [60]fullerene complex. The numbers indicate the chemical shifts ($\Delta\delta_H$): 600 MHz, $Cl_2CDCDCl_2$, 60°C, [**3**]=0.50 mmol dm^{-3}, ([60]fullerene)=5.3 mmol dm^{-3}. The numbers in parentheses denote the shift from uncomplexed **3** (+ to lower magnetic field, − to higher magnetic field). [a]The chemical shift of the ArH protons of calixarene overlaps with those of other aromatic protons.

chemical-shift change induced by **2** suggests that the weak and rapidly-exchangeable interaction may be operative between **2** and [60]fullerene.

The ^1H NMR spectrum of **3** in the presence of [60]fullerene is shown in Fig. 1. The proton signals for free **3** and those for **3**·[60]fullerene complex appeared separately, and these signals were not coalesced even at 90°C. At 60°C the assignment (Fig. 3) was successfully attained using the ^1H–^1H COSY spectrum. It is known that the angle of the phenyl units against the calixarene ring plane can be estimated by the chemical shift difference ($\Delta\delta_H$) between axial and equatorial protons in the $ArCH_2O$ methylene groups.[6,22] In the absence of [60]fullerene the $\Delta\delta_H$ of **3** was 0.56 ppm. This value is close to that of **4** (0.48 ppm, 30°C, toluene-d_8: CD_3OD=44:1 v/v). In contrast, the $\Delta\delta_H$ of the **3**·[60]fullerene complex was increased to 0.72 ppm, which is similar to that of the **4**·Li^+ complex (0.68 ppm, 30°C, toluene-d_8: CD_3OD=44:1 v/v) which has the flattened phenyl groups suitable to inclusion of [60]fullerene in the cavity.[6] These results indicate that to interact with [60]fullerene, the phenyl groups in **3** must be also flattened to create a cavity shape suitable to inclusion of [60]fullerene (Fig. 4). The signals observed for the **3**·[60]fullerene complex imply that even after including [60]fullerene **3** maintains a D_{3h}-symmetrical structure. The α- and β-pyridyl proton signals for free **3** appeared as a 'singlet' at 8.80 and 7.08 ppm, respectively. A priori, each of the α- and β-proton has two inequivalent protons, viz. exo-annulus one and endo-annulus one. This result indicates, therefore, that at 60°C these inequivalent protons are averaged because of the rotation of the pyridine rings faster than the ^1H NMR time-scale.[23] In contrast, the α- and β-pyridyl proton signals for the **3**·[60]fullerene complex appeared separately, indicating that the rotation of the pyridine rings becomes slower than the ^1H NMR time-scale. The change in the rotational speed is ascribed to 'steric hindrance' arising from included [60]fullerene. The large down-field shift observed for one α- and one



3

3·[60]fullerene complex

Figure 4. Flattening of homooxacalix[3]arene units induced by [60]fullerene inclusion.

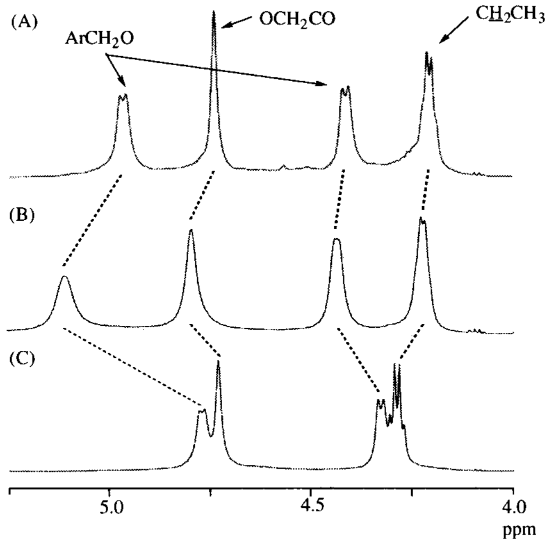


Figure 5. ^{1}H NMR chemical shifts for selected Cl$_2$CDCDCl$_2$, 25°C, (A) [**3**]=2.5 mmol dm^{-3}, (B) [**3**]=2.5 mmol dm^{-3}, [CF$_3$SO$_3$Li]=15 mmol dm^{-3}, (C) [**3**]=2.5 mmol dm^{-3}, [CF$_3$SO$_3$Na]=10 mmol dm^{-3}.

β-pyridyl proton (+0.13 and +0.78 ppm, respectively) suggests that these protons are affected by the π electron ring current of the included [60]fullerene. The association constants (K_{ass}) could be readily estimated from the ratio of the peak intensity of free **3** and the **3**·[60]fullerene complex in the ^{1}H NMR spectra to be 39 dm^3 mol^{-1} at 30°C and 54 dm^3 mol^{-1} at 60°C.[24]

K_{ass} improvement by the Li$^+$-binding

We previously found that OH-unmodified homooxacalix[3]arene can include [60]fullerene whereas its derivative, **4**, cannot interact with [60]fullerene.[6] The difference was explained by the difference in the inclination angle of the phenyl groups: that is, OH-unmodified homooxacalix[3]arene provides a proper angle for the phenyl groups to enjoy the multi-point interaction with [60]fullerene whereas the phenyl groups in **4** stand up too much and the insertion of [60]fullerene into the narrowed cavity becomes very difficult.[6] Very interestingly, it was found that **4** interacts with [60]fullerene when it is converted to the Li$^+$ complex.[6] The ^{1}H NMR studies established that the phenyl groups in the Li$^+$ complex are more flattened than those in **4** so that three ethoxycarbonylmethoxy groups can interact with bound Li$^+$. As a result, the angle is nearly comparable with that of OH-unmodified homooxacalix[3]arene.[6] The finding stimulated us to add Li$^+$ to the **3** + [60]fullerene system, because the phenyl groups may be more flattened by the Li$^+$-binding and may provide a cavity more suitable to the [60]fullerene binding.

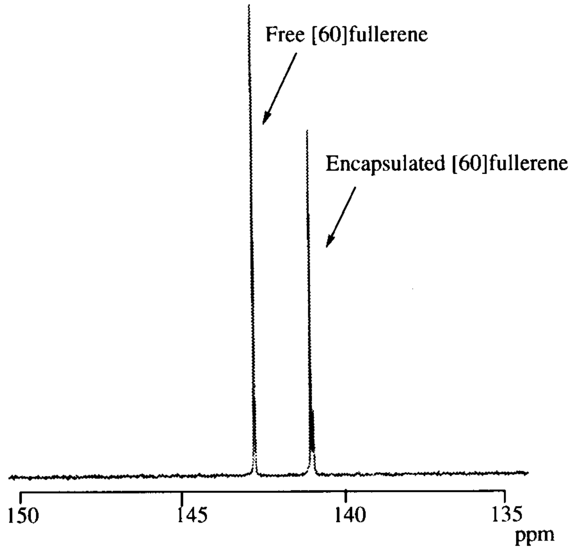


Figure 6. Partial ^{13}C NMR spectrum of ^{13}C-enriched [60]fullerene (2.5 mmol dm^{-3}) in the presence of **3**·(Li$^+$)$_2$ (1.25 mmol dm^{-3}): 150 MHz, Cl$_2$CDCDCl$_2$, 25°C.

Since **3** possesses two strong Li$^+$-binding sites, one may presume that the **3**·(Li$^+$)$_2$ 1:2 complex is formed in the presence of excess Li$^+$. We thus measured the ^{1}H NMR spectra of **3** (2.5 mmol dm^{-3}) as a function of the CF$_3$SO$_3$Li concentration. It was confirmed that the chemical shift change is saturated to a plateau above [CF$_3$SO$_3$Li]/[**3**]>3.0. Hence, the [CF$_3$SO$_3$Li$^+$]/[**3**]=6.0 ratio was chosen as a major measurement condition.[25] From the similar experiment for CF$_3$SO$_3$Na, the [CF$_3$SO$_3$Na]/[**3**]=4.0 ratio was chosen for Na$^+$.[25]

In Fig. 5, the δ_H values for selected protons and the $\Delta\delta_H$ values for H_{ax} and H_{eq} for the ArCH$_2$O methylene protons are compared. It is seen from Fig. 5 that the $\Delta\delta_H$ for the **3**·(Li$^+$)$_2$ complex (0.73 ppm) is greater than that for **3** (0.56 ppm). This implies that the phenyl groups in the **3**·(Li$^+$)$_2$ complex are flattened for the ethoxycarbonylmethoxy groups to interact with 'small' Li$^+$ cations.[6] Further important is the fact that this $\Delta\delta_H$ is very close to that for the **3**·[60]fullerene complex (0.72 ppm): that is, the dimeric capsule has been preorganized for [60]fullerene inclusion by the Li$^+$-binding. One can expect, therefore, that the K_{ass} would be enhanced in the presence of CF$_3$SO$_3$Li. On the other hand, the $\Delta\delta_H$ for the **3**·(Na$^+$)$_2$ complex (0.45 ppm) is smaller than that for **3** (0.56 ppm). This indicates that the phenyl groups further stand up when the ethoxycarbonylmethoxy groups interact with 'large' Na$^+$ and the dimeric capsule has become more elliptic.[6] One can expect, therefore, that the K_{ass} would be decreased in the presence of CF$_3$SO$_3$Na.

Here, we measured ^{1}H and ^{13}C NMR spectra to evaluate whether the **3**·Li$^+$ complex really shows the enhanced affinity with [60]fullerene. In the ^{13}C NMR spectrum using ^{13}C-enriched [60]fullerene (^{13}C content, ca. 12%) (Fig. 6), a new separate peak assignable to the **3**·(Li$^+$)$_2$·[60]fullerene complex appeared at 141.09 ppm and the relative intensity was much stronger than that for the **3** + [60]fullerene system (Fig. 2). In the ^{1}H NMR spectrum (Fig. 7), several new peaks assignable to the **3**·(Li$^+$)$_2$·[60]fullerene complex appeared separately from those assignable to the **3**·(Li$^+$)$_2$ complex. From the integral intensity ratio of these two species in the ^{1}H NMR spectra the K_{ass} for the formation of the **3**·(Li$^+$)$_2$·[60]fullerene complex from **3**·(Li$^+$)$_2$ and [60]fullerene (Fig. 8) was estimated to be 2100 dm^3 mol^{-1} at 30°C. Thus, the K_{ass} is enhanced by a factor of ca. 54 by the Li$^+$-induced

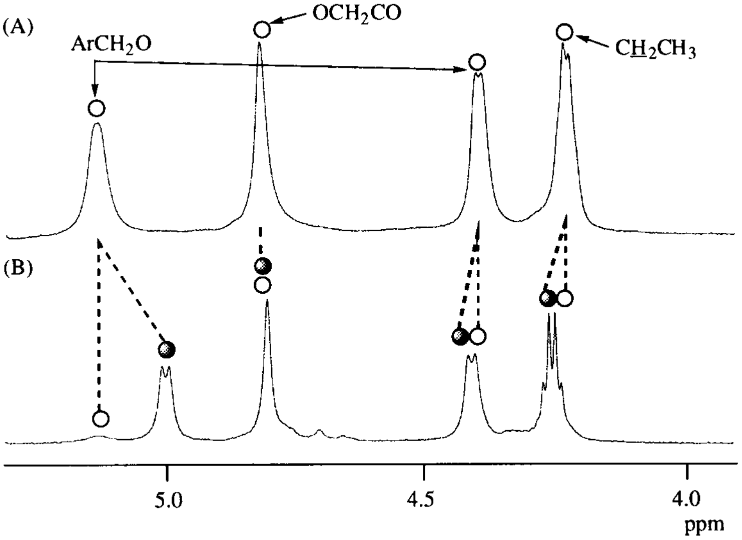


Figure 7. Partial ^{1}H NMR spectra of (A) $\mathbf{3}\cdot(Li^+)_2$ (1.25 mmol dm^{-3}) and (B) $\mathbf{3}\cdot(Li^+)_2$+[60]fullerene (2.5 mmol dm^{-3}): 600 MHz, $Cl_2CDCDCl_2$, 25°C. ● and ○ indicate the peaks assignable to $\mathbf{3}\cdot(Li^+)_2$ and $\mathbf{3}\cdot(Li^+)_2$+[60]fullerene, respectively.

preorganization of the dimeric capsule. The marked increase in the K_{ass} indicates the importance of the preorganization effect on the [60]fullerene inclusion.

The complexation ability of the $\mathbf{3}\cdot(Na^+)_2$ complex for [60]fullerene was also evaluated utilizing the ^{1}H and ^{13}C NMR spectroscopic measurements. However, neither the appearance of new NMR peaks nor the peak shift of the $\mathbf{3}\cdot(Na^+)_2$ complex was induced by [60]fullerene addition. One may consider, therefore, that the elliptic inner cavity is not suitable to the [60]fullerene-binding. Judging from resolution and sensitivity of the NMR apparatus used herein, the fact that the peak is virtually undetectable implies that the K_{ass} (if any) is smaller than 5 dm^3 mol^{-1}.

Here, it occurred to us that such an elliptical cavity might be suitable to capture oval-shaped [70]fullerene because of the 'hole-shape complementarity'. We thus repeated the ^{1}H and ^{13}C NMR spectroscopic measurements for [70]fullerene. Contrary to our expectation, none of **3**, $\mathbf{3}\cdot(Li^+)_2$ and $\mathbf{3}\cdot(Na^+)_2$ showed the NMR spectral change attributable to the [70]fullerene-binding. Again, the K_{ass} values (if any) are estimated to be smaller than 5 dm^3 mol^{-1}. It seems to be a little strange that even though, **3**, $\mathbf{3}\cdot(Li^+)_2$ and $\mathbf{3}\cdot(Na^+)_2$ provide the cavities preorganized to the various shapes, [70]fullerene is scarcely bound to these cavities. This suggests that as pointed out by Atwood,[14] not only the hole-shape complementarity but also the molecular symmetry complementarity may be also taken into consideration in order to efficiently bind [70]fullerene. In fact, there are a few precedents which report successful [70]fullerene inclusion.[26] We do not know whether these examples fully satisfy both of these two complementarities or not. The basic prerequisites for [60]fullerene have thoroughly been discussed through screening of many available calixarenes. We now consider that the similar investigation should be conducted to establish the fundamental prerequisites for [70]fullerene inclusion.

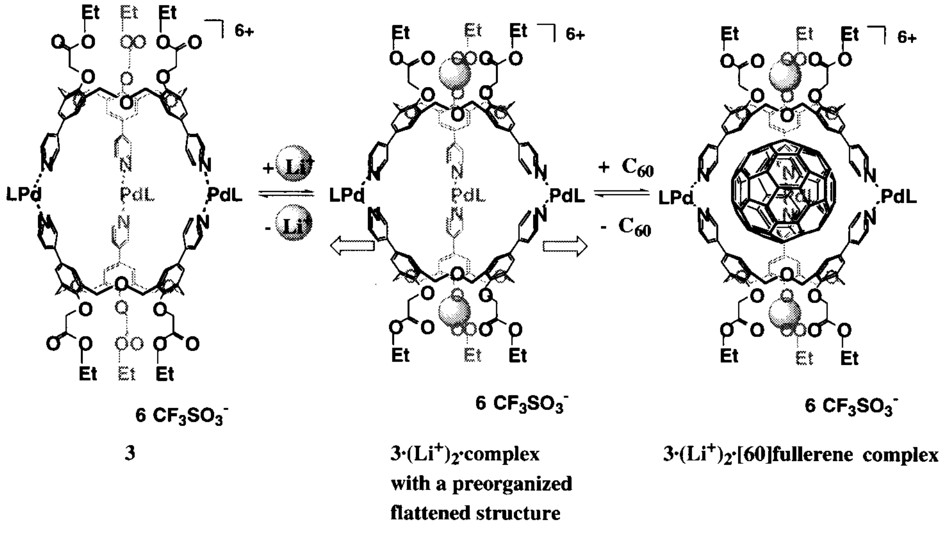


Figure 8. Association of [60]fullerene with $\mathbf{3}\cdot(Li^+)_2$ consisting of the flattened phenyl groups.

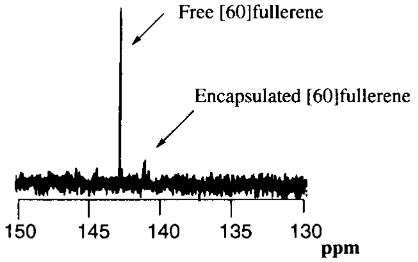


Figure 9. Partial ^{13}C NMR spectrum after addition of excess CF_3SO_3Na: for the measurement conditions see Fig. 6.

Switching of [60]fullerene inclusion by the Na^+-binding

As mentioned above, the Li^+-binding to the lower rims enhances the [60]fullerene inclusion ability of **3** whereas the Na^+-binding to the lower rims removes it entirely. The finding implies that the inclusion property of **3** can be switched from a [60]fullerene receptor in the presence of Li^+ to an incompetent receptor in the presence of excess Na^+ by replacement of bound Li^+ with excess Na^+. The feasibility of this idea was tested by monitoring metal-conjugated decomplexation of [60]fullerene by ^1H and ^{13}C NMR spctroscopy.

To a solution containing a $\mathbf{3}\cdot(Li^+)_2\cdot$[60]fullerene complex ([[60]fullerene]=2.5 mmol dm^{-3}, $[\mathbf{3}\cdot(Li^+)_2]$1.25 mmol dm^{-3}) which gave a ^{13}C NMR spectrum in Fig. 6 was added excess CF_3SO_3Na (as a solid) and the mixture was sonicated at room temperature for 30 min. After filtration, the filtrate was subjected to the ^{13}C NMR measurement. As expected, the peak intensity ratio of complexed versus free [60]fullerene (0.7:1.0 in Fig. 6) decreased to (0.1:1.0 as shown in Fig. 9). Although a weak peak assignable to the complexed [60]fullerene was still observable in Fig. 9, the ^1H NMR spectrum was nearly same as that of the $3\cdot(Na^+)_2$ complex. As a summary of the foregoing findings, one may propose that by replacement of Li^+ with Na^+ at the lower rims [60]fullerene is released out of the supramolecular cavity in **3** (Fig. 10).

Conclusion

In conclusion, the present paper demonstrated a novel system for the inclusion of [60]fullerene in a capsule-like cage molecule. In particular, this is the first example that included [60]fullerene gives the separate ^1H and ^{13}C NMR peaks, indicating that the exchange rate is slower than these NMR time-scales. In addition, the K_{ass} can be remarkably enhanced by preorganization utilizing the Li^+-binding to the lower rims. Also important implication is that not only the covalent bond and the hydrogen-bonding interaction but also the coordination bond provides a promising strategy to construct capsule-like cage molecules from calixarenes. The cage molecule can disrupt [60]fullerene–solvent and [60]fullerene–[60]fullerene interactions, so that: (i) one may estimate 'unimolecular' chemical and physical properties of [60]fullerene in polar solvents, (ii) one may inhibit undesired photo-dimerization of [60]fullerene, or (iii) only the specific substrate which can pass through the windows of the cage molecule may react with [60]fullerene. One may consider that the size and the shape of the windows may be also changed by the metal-binding. We believe that further modification of the size and the shape of the capsule would lead to further extension of this research related to selective binding of higher fullerenes.

Experimental

Miscellaneous

Melting points were determined on a Micro Melting Point Apparatus (Yanaco MP-500D) and uncorrected. ^1H and ^{13}C NMR spectra were measured on a Bruker DRX 600 spectrometer.

Materials

The syntheses of compounds **2**[16b] and **4**[6] were described previously.

Preparation of 7,15,23-tri-*p*-pyridyl-25,26,27-tris[(ethoxycarbonyl)methoxy]-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene (1)

7,15,23-Tribromo-25,26,27-tris[(ethoxycarbonyl)methoxy]-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene[6] (0.20 g, 0.25 mmol) was dissolved in 20 ml of a 1,2-dimethoxyethane and to this solution were added diethyl(4-pyridyl)borane (0.11 g, 0.73 mmol), cesium fluoride (0.20 g, 1.32 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.02 g, 0.02 mmol). The mixture was stirred at the reflux temperature for 5 h. After cooling, the reaction

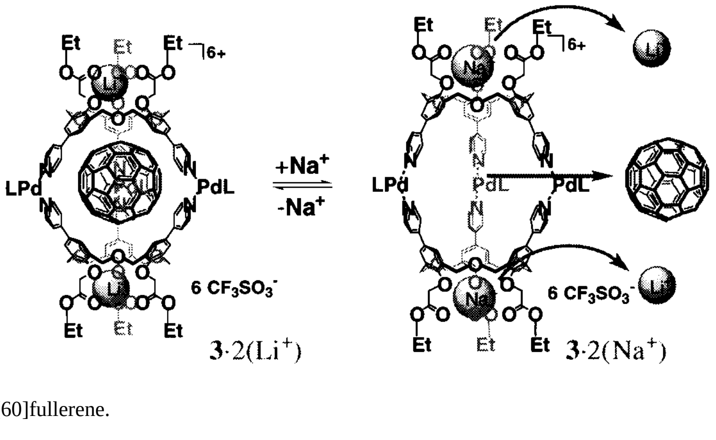


Figure 10. Na^+-induced release of [60]fullerene.

mixture was filtered and the filtrate was washed twice with water and dried over $MgSO_4$. After evaporation to dryness, the residue was purified by preparative TLC on silica gel using acetone:ethanol:chroloform, 1:1:10 (v/v/v) as an eluent: yield, 32%; mp 115–117°C; ^{1}H NMR (600 MHz, $Cl_2CDCDCl_2$): δ/ppm 1.35 (t, 3H, CH_2CH_3); 4.29 (q, 2H, CH_2CH_3); 4.55 (s, 2H, $ArOCH_2$); 4.64 and 4.95 (each d, each 2H, $ArCH_2O$); 7.08 (d, 2H, Pyl-H(α)); 7.18 (s, 2H, ArH); 8.40 (d, 2H, Pyl-H(β)); Anal. Calcd for $C_{51}H_{51}O_{12}N_3\cdot 0.5\ CHCl_3$: C, 67.49; H, 5.66; N, 4.62. Found; 67.67; H, 5.83; N, 4.58.

Acknowledgements

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1:2 complex and free **3** in $Cl_2CDCDCl_2$ at 0°C. When the ratio was higher ($[CF_3SO_3Na^+]/[$**3**$]=4.0$), the simple splitting pattern was obtained, which was assignable to the 1:2 complex with D_{3h}-symmetry. For the Li^+ complex such a clear peak splitting was not observed in ^1H NMR spectroscopy but the chemical shifts changed toward the saturation. Since there is no reason why the Li^+ binding must be saturated at the 1:1 stoichiometrical stage, one can consider that the **3**/Li^+ 1:2 complex is formed in the presence of excess $CF_3SO_3Li^+$.

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