

Novel interactions of calixarene π -systems with metal ions and fullerenes*

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Abstract: This review article introduces encounters of calixarenes with fullerenes (particularly, with [60]fullerene) in the solid state, in solutions, and in the covalently linked conjugates. The starting point of this chemistry is the accidental finding that calix[8]arenes selectively include [60]fullerene in carbon soot and give the precipitate with 1:1 stoichiometry. It is shown that calixarenes not only behave as a unique receptor for fullerenes but also are useful to modify the functions inherent to the fullerene π -systems.

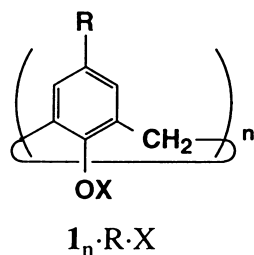
Calixarenes [1] appeared as the third generation of supramolecular host compounds after cyclodextrins and crown ethers, whereas fullerenes [2] appeared as the third generation of carbon clusters after graphites and diamonds. Since calixarenes have a cavity composed of benzene rings while fullerenes are buckyballs covered by π -electrons, these two third generations may have a chance to get married to each other, e.g. through π - π interactions. This expectation has become actual by an accidental finding by Atwood *et al.* [3] and by us [4] that calix[8]arenes selectively include [60]fullerene in carbon soot and form the precipitate with 1:1 stoichiometry. In this review article, we survey the calixarene chemistry aiming at such calixarene–fullerene conjugates.

It is known that the interaction of [60]fullerene with electron-rich aromatic compounds results in the formation of crystals, in which [60]fullerene directly contact the π -faces of the aromatics[5,6]. One may thus expect that electron-rich aromatic compounds, particularly, those with macrocyclic π -systems would form complexes with [60]fullerene and other fullerene homologues even in solution. We thus considered that introduction of an electron-rich structural unit into a macrocycle would create a new macrocyclic [60]fullerene receptor. Since the inner cavity size of calix[8]arenes is comparable with the size of [60]fullerene, we decided to introduce the eight 3,5-dimethoxyphenyl structural units into *p*-*tert*-butylcalix[8]arene (**1**₈·Bu^t·H) [7]. Although this compound did not give any indication of the complex formation with [60]fullerene, we unexpectedly found that the starting material, **1**₈·Bu^t·H, treated with [60]fullerene in toluene formed a precipitate having 1:1 **1**₈·Bu^t·H/ [60]fullerene stoichiometry. We immediately applied this system to carbon soot and eventually found that **1**₈·Bu^t·H selectively ‘includes’ [60]fullerene among a mixture of fullerene homologues and forms a precipitate from toluene [4]. Highly pure [60]fullerene can be recovered from this precipitate by dispersing this 1:1 complex into chloroform [4]. A similar finding was published concurrently by the Atwood’s group [3] (Scheme 1).

The survey of the past references taught us that the charge–transfer interaction with *N,N*-dialkylaniline derivatives is the sole non-covalent interaction useful to capture [60]fullerene in organic solvents [8]. Therefore, we decided to introduce *N,N*-dialkylaniline units or *m*-phenylenediamine units into calix[*n*]arenes. When they are introduced into the upper rim of a calix[6]arene, the size of the thus extended cavity becomes comparable with that of a calix[8]arene. Furthermore, the treatment of a calix[6]arene is much easier than that of a calix[8]arene. Taking these advantages into consideration, we designed and synthesized **2**Dod and **3** and compared their K_{ass} values with those of reference compounds

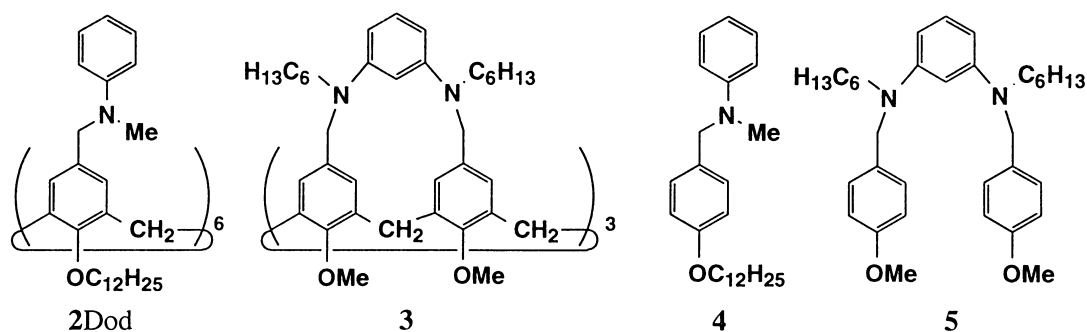
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Scheme 1

4 and **5** [9]. The K_{ass} values determined in toluene from the absorption spectroscopic change were 7.9/M for **2Dod**, 110/M for **3**, 0.20/M for **4**, and 0.43/M for **5**. Comparison of the data for **2Dod** ~ **5** establishes that K_{ass} of reference compound **5** is only twofold larger than that of **4**, whereas the K_{ass} of the host compound **3** is 14-fold larger than that of **2Dod**. The large K_{ass} enhancement of **3** relative to **2Dod** is accounted for by: (i) the stronger donation ability of the *m*-phenylenediamine unit relative to the *N,N*-dialkylaniline one, and (ii) the higher preorganization brought about by stapling two calix[6]arene phenyl units. The proposed structure including the cooperative action of donor groups is shown in Fig. 1. These results successfully demonstrate that stable inclusion complexes of [60]fullerene in solution can be formed with host molecules in which donor groups such as *N,N*-dialkylaniline or *m*-phenylenediamine are preorganized on an appropriate platform. Undoubtedly, calix[6]arene is one of the best platforms for this purpose (Scheme 1; Fig. 1).



Scheme 2

More recently, Atwood *et al.* [10] found that excess cyclotrimeratrylene (CTV: **6**) and [60]fullerene in toluene results in micelle-like aggregation of the fullerenes which is spectrophotometrically detectable. This implies that the CTV-[60]fullerene interaction is not so strong as to disperse [60]fullerene particles discretely into toluene solution but does exist even in toluene solution. This finding has stimulated us to screen the potential inclusion ability of many calixarene derivatives we have synthesized so far. After

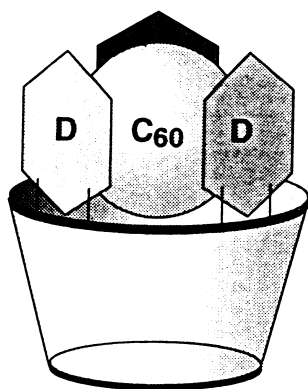


Fig. 1 Proposed structure including the cooperative action of donor groups.

examination of 28 calixarene derivatives we have eventually discovered that OH-unsubstituted calix[5]arenes ($1_5\cdot R\cdot H$), calix[6]arenes ($1_6\cdot R\cdot H$), and homooxacalix[3]arenes ($7\cdot R\cdot H$) do interact with [60]fullerene in toluene [11]. The K_{ass} determined in toluene from the absorption spectroscopic change was 35/M for $7\cdot\text{Bu}^t\cdot H$. These findings support the view that [60]fullerene is included by a few selected calixarenes. From the extensive screening we can now conclude that the primary prerequisite for [60]fullerene inclusion is that the OH groups on the lower rim are not substituted so that they can adopt a cone conformation. The secondary prerequisite is the ring size that the interaction is observed only for unmodified calix[5]arene, calix[6]arene, and homooxacalix[3]arene but not for calix[4]arene. Previously, we theoretically estimated the most stable conformations of unmodified calix[n]arenes [12], which showed good agreements with those determined by X-ray crystallographic analyses [13,14]. From comparison of the structure of the stablest conformers with the [60]fullerene globular structure we noticed that the cavities of these calixarenes are too small to deeply 'include' [60]fullerene but have an inclination of the benzene rings apt to enjoy a multipoint contact with the [60]fullerene surface: that is, they can interact as a partial 'cap' for [60]fullerene (Fig. 2). This requirement is also satisfied by $7\cdot\text{Bu}^t\cdot H$. This second prerequisite allows us to consider that the major driving-force for [60]fullerene inclusion is a π - π interaction (including the charge-transfer-type interaction) and/or a solvophobic effect. To fully enjoy this effect calix[n]arenes are required to be preorganized in a cone conformation through intramolecular hydrogen-bonds among OH groups.

Fukazawa *et al.* [15] also found that OH-unsubstituted calix [5] arenes can include [60]fullerene in toluene. A calix [5] arene with two iodide groups and three methyl groups at the *para*-positions gave $K_{\text{ass}} = 2120/\text{M}$. The X-ray crystallographic analysis showed that one [60]fullerene is sandwiched by two calix[5]arene cavities [16] (Fig. 2).

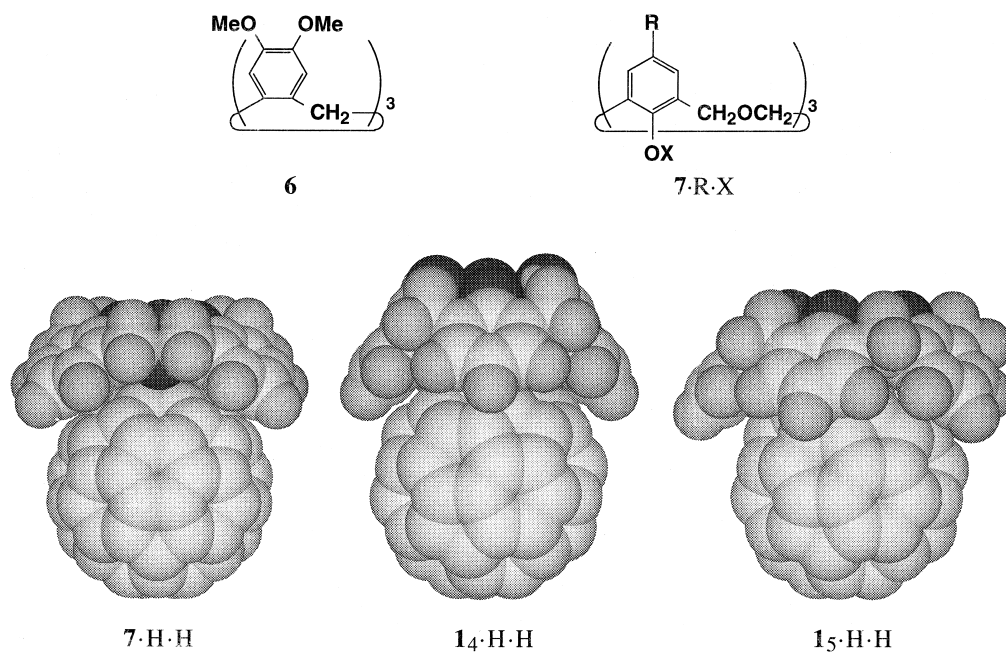


Fig. 2 Interaction of energy-minimized [with MM3 (92)] $7\cdot H\cdot H$, $1_4\cdot H\cdot H$, and $1_5\cdot H\cdot H$ with [60]fullerene. $1_5\cdot H\cdot H$ can provide a benzene ring inclination suitable to [60]fullerene-binding whereas the upper-rim edge of $1_4\cdot H\cdot H$ is too narrow to accept [60]fullerene.

It is known that the conformational freedom remaining in calixarene ester derivatives ($1_n\cdot R\cdot\text{Es}$ and $7\cdot R\cdot\text{Es}$ where Es denotes CH_2COOEt) can be frozen to a cone conformation by complexation with appropriate metal cations [17,18]. Therefore, if the above proposals are correct, the conformationally mobile ester derivatives should not interact with [60]fullerene whereas their metal-frozen cone conformers should include [60]fullerene. To test this intriguing hypothesis we thoroughly investigated spectroscopic properties of [60]fullerene in the presence of $7\cdot R\cdot\text{Es}$ (where $R = \text{Bu}^t$, Me and Br) and $1_n\cdot\text{Bu}^t\cdot\text{Es}$ (where $n = 4$ and 6). We confirmed that the calix[n]aryl esters become able to interact with

[60]fullerene only when they are appropriately preorganized into a cone conformation by complexed metal cations [19]. The typical metal complexes which accept [60]fullerene are $1_6\text{-Bu}^t\text{-Es} + \text{Cs}^+$ and $7\text{-Bu}^t\text{-Es} + \text{Li}^+$. $1_6\text{-Bu}^t\text{-Es}$ tends to adopt a 1,2,3-alternate conformation while it changes into a C_{3v} -symmetrical cone in the presence of Cs^+ (Fig. 3) [17]. $7\text{-Bu}^t\text{-Es}$ is immobilized in a cone but the ether-containing ring is flexible. Li^+ bound to the lower-rim ester-groups restricts the molecular motion and rigidifies the cone skeleton [18]. Furthermore, the ^1H NMR spectroscopic studies showed that the inclination angles of $1_6\text{-Bu}^t\text{-Es} + \text{Cs}^+$ and $7\text{-Bu}^t\text{-Es} + \text{Li}^+$ are very close to those of $1_6\text{-Bu}^t\text{-H}$ and $7\text{-Bu}^t\text{-H}$,²⁶ respectively, which can accept [60]fullerene [11,15] (Fig. 3).

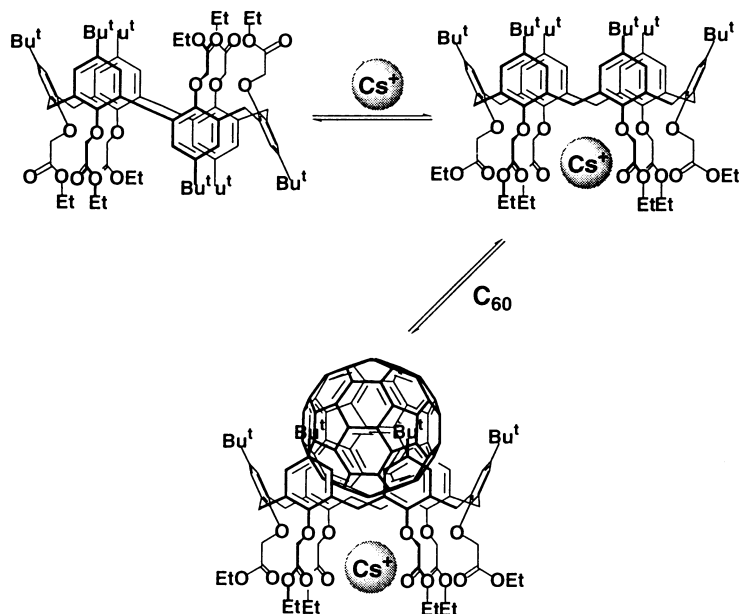


Fig. 3 Conformational change of $1_6\text{-Bu}^t\text{-Es}$ after formation of a complex with Cs^+ and creation of a cone cavity for [60]fullerene inclusion.

We recently found that cone-7-Py-Es self-assembles into a dimeric capsule molecule in the presence of PdL^{2+} (Fig. 4) [20]. Very interestingly, we found unequivocal evidence that [60]fullerene is encapsulated in this cavity. In $\text{CDCl}_2\text{CDCl}_2$ at 25°C , a mixture of [60]fullerene (5.8 mM; ^{13}C -enriched) and **8** [20] (5.0 mM) gave two separate peaks at 142.87 and 140.97 p.p.m. in ^{13}C NMR spectroscopy. The peak at higher magnetic field is ascribable to [60]fullerene included in the cavity of **8** (Fig. 5). From the ratio of the ^1H NMR peak intensity the K_{ass} was estimated to be 54M^{-1} at 60°C [20]. To the best of our knowledge, this is the first example for encapsulation of [60]fullerene in a cage compound.

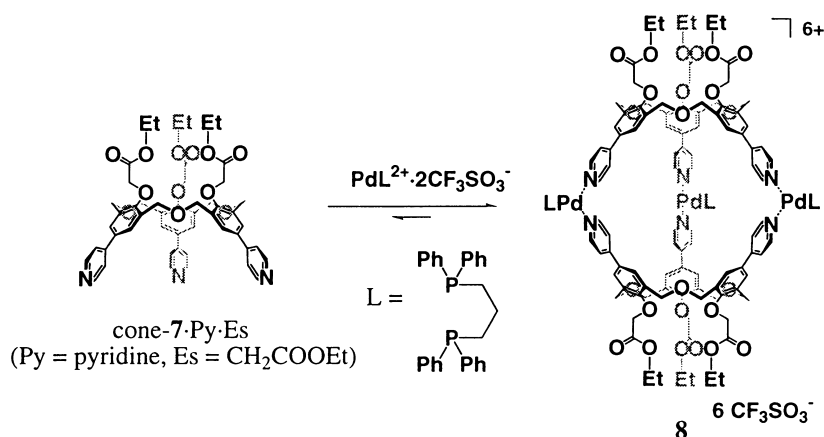


Fig. 4 Proposed structure of **8** which consists of $[\text{cone-7-Py-Es}]:[\text{PdL}] = 2:3$ complex.

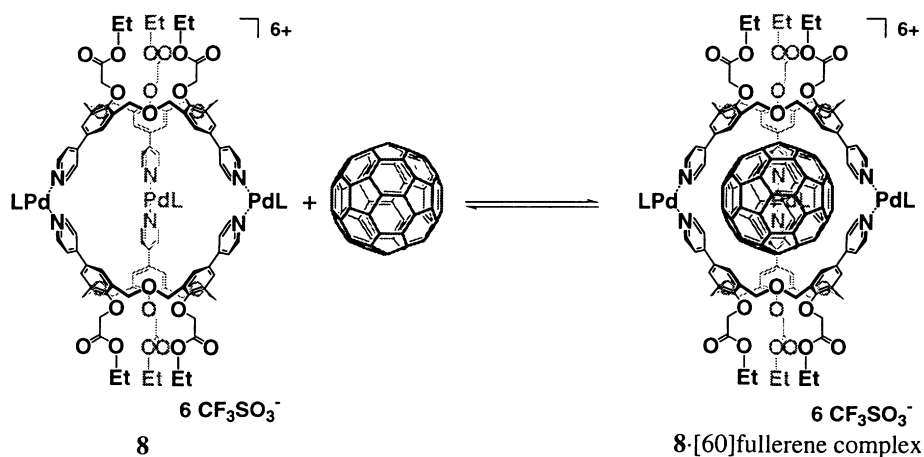
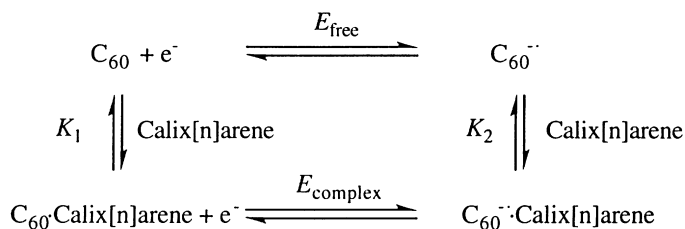


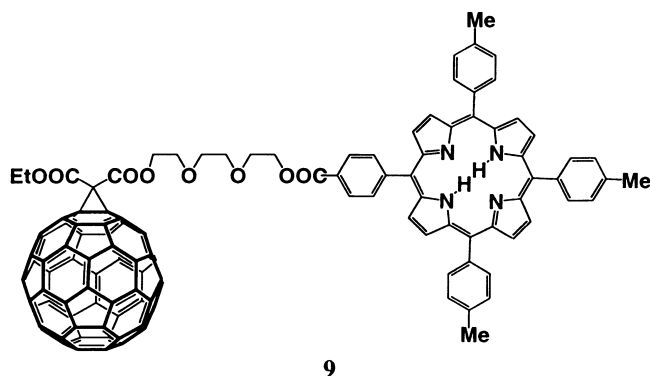
Fig. 5 Proposed structure of an 8·[60]fullerene complex.

Bard *et al.* [21] have found that the $1_8\text{-Bu}^1\text{-H}$ ·[60]fullerene complex (solid) embedded in the electroconductive polymer membrane tends to be dissociated when it is electrochemically reduced. The finding suggests that the charge-transfer-type interaction is one of the driving-forces for [60]fullerene inclusion. [60]Fullerene-calix[*n*]arene interactions in solution were studied in toluene:MeCN = 10:1 (v/v) by an electrochemical method [22] (Scheme 3). The results are quite complementary to those obtained from a spectroscopic method: i.e. in the presence of $7\text{-Bu}^1\text{-H}$ and $1_5\text{-Bu}^1\text{-H}$, both E_{red} and E_{ox} shifted to the negative potential whereas they were scarcely affected by the addition of 1_4-H-H . The K_2 values electrochemically determined for the association with $\text{C}_{60}^{\cdot-}$ are generally smaller than the K_1 values spectroscopically determined for the association constant with [60]fullerene. The tendency indicates that the $\text{C}_{60}^{\cdot-}$ is partially dissociated and the charge-transfer-type interaction is one of the driving-forces for [60]fullerene inclusion in solution.



Scheme 3

Compound **9** has a porphyrine moiety as a fluorophore [23]. From the data for calix[*n*]arene titrations, monitored *via* the fluorescence spectra, the K_{ass} values for calix[*n*]arenes- [60]fullerene complexes were determined [24]. The similar results were obtained from the UV-Vis spectra (Scheme 4).



Scheme 4

CONCLUSION

The foregoing studies have demonstrated that such calix[*n*]arenes that have a preorganized cone conformation and a proper inclination of the benzene rings can interact with [60]fullerene even in solution. This means that deep inclusion of [60]fullerene into the calix[*n*]arene cavity, as expected for calix[8]arenes, is not necessarily a prerequisite for [60]fullerene inclusion. We believe that the present results will open a door to new host-guest chemistry between fullerenes and calix[*n*]arenes.

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