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Review Article

Supramolecular Adducts and Aggregates – An Overview

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Abstract

Review of the host–guest chemistry of supramolecules including fullerenes is illustrated here. Host molecules like cyclodextrins, Crown ethers, Calix[n]arenes, Resorcin[n]arenas, Tribenzotriquinacenes, azobenzene, dendrimers etc. incorporate guest molecules like mytomycine C (drug molecule), metal ions, fullerenes into the cavity of its core unit. Inclusion of fullerenes occurs not only by van der Waals interactions but also, in some cases, via p-electronic charge-transfer from the host moieties to the guest fullerenes. The conformational flexibility of the host molecule affects the own cavity size and thus hinders inclusion complex formation. The complexation phenomenon may be utilised to dissolve the fullerenes in the non-toxic vitamin A oil and the solution may be used for testing the biological activity of the fullerenes *in vivo*. Extraction of fullerenes from carbon soot can be possible using selective host molecules by inclusion complex formation. Cavitant molecules behave like a surfactants depending upon the environment. Formation constant with fullerene changes with change of critical micellization constant. [60]fullerene aggregates in water and all experimental and theoretical evidences support that the aggregates contain $(C_{60})_{13}$ units. Minima of the previously reported energy calculations and in the work reported in this chapter they have been shown to be a natural consequence of stacking of cuboctahedra made up of C_{60} molecules. A Young diagram like method has been developed for counting the number of C_{60} molecules in these cuboctahedral stacks. Hence this article would review the application and explore of supra molecular host-guest complex and aggregates on various recent research works.

Keywords: Host-guest complex, Aggregate, Fullerene, drug delivery, Molecular recognition

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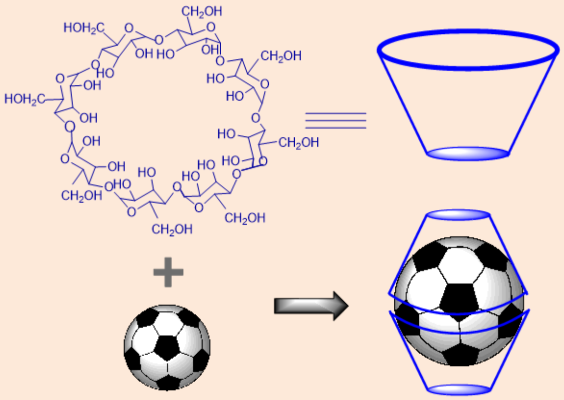

Introduction

The terms ‘molecular complexes’, ‘inclusion or host-guest complexes’ and ‘charge transfer (or electron donor-acceptor) complexes’, have been and are still being used widely in the literature [1-9]. The intention of using the word ‘molecular adducts’ in the present dissertation is to include all these substances where a small (2 to 3) number of molecules are held together by weak (non-covalent) intermolecular forces. Although ‘adducts’ in general mean products of addition reactions and a large number of such reactions involve transformation of π-bonds into σ-bonds, such cases have not been dealt with in the present dissertation. To be specific ‘molecular adducts’ in this dissertation will mean those formed by non-covalent intermolecular interactions. The terms ‘molecular complexes’ and molecular adducts' will be used synonymously. The term 'aggregates' is used to mean molecular clusters having a fairly large number of molecules bound by forces generally encountered in surface and colloid chemistry.

Molecular Adducts

In this section two main types of molecular adducts and their applications will be discussed briefly.

Electron donor-acceptor or charge transfer complexes

Organic electron donor-acceptor (EDA) or charge-transfer (CT) complexes are loose molecular associations of two different molecules such that absorption of light in the UV/Vis range is accompanied by an appreciable transfer of an electron from the highest occupied molecular orbital (HOMO) of one molecule (called 'donor') to the lowest unoccupied molecular orbital (LUMO) of the other (called 'acceptor'), although in most cases there is very little electron (charge) transfer in the ground state of the molecular complex. A well known example of such a complex is the naphthalene-*p*-chloranil adduct which has a beautiful red colour in carbon tetrachloride solution, although the component substances are colourless (naphthalene) or very faintly yellow (*p*-chloranil). According to Mulliken's theory [10, 11], the ground and excited states of an EDA complex are given by the wave functions

$$\psi_G = a\,\psi_0\,(D \ldots A) \;+\; b\,\psi_1\,(D^+ - A^-), \qquad a \gg b \qquad \ldots(1.1)$$

$$\psi_E = a^*\,\psi_1\,(D^+ - A^-) - b^*\psi_0\,(D \ldots A), \qquad a^* \gg b^* \qquad \ldots(1.2)$$

where ψ_0 ($D\ldots A$) is the wave function of a 'no bond' structure ($D\ldots A$) and ψ_1 ($D^+ - A^-$) is that of a 'dative' structure ($D^+ - A^-$). The 'no bond' structure means that the donor and acceptor molecules are held together by van der Waals types of forces and hydrogen bonds (where possible). The 'dative' structure means that one electron is completely transferred from the donor molecule to the acceptor molecule and the resulting ions are held together predominantly by electrostatic attraction. Equations (1.1) and (1.2) imply that both in the ground and excited states the actual structure of the EDA complex is a resonance hybrid of the 'no bond' and 'dative' structures, the former predominating in the ground state and the latter in the excited state. The energy ($h\nu_{CT}$) required for the transition

$$\psi_G \xrightarrow{h\nu_{CT}} \psi_E$$

is called 'charge transfer transition energy' and it usually belongs to the UV or visible region of electromagnetic radiation. Experimentally, the formation of an EDA complex on mixing together the solutions of donor and acceptor is indicated by (i) the appearance of a new colour or a new absorption band in the UV region different from the absorption bands of the component substances and (ii) formation of no new compound other than the adduct whose formation constant (K) can be determined from the equation

$$K = \frac{[AD]}{[A][D]} \qquad \ldots(1.3)$$

where square brackets denote the concentrations of the species enclosed after establishment of equilibrium,

$$A + D \rightleftharpoons AD$$

Organic charge transfer complexes have been found to be of great technological utility. For example, in the solid state some EDA complexes have been found to be electrically conducting. Thus, [12-14] the complex between tetracyanoquinodimethane (TCNQ, an electron acceptor) and tetrathiafulvalene (TTF, a good π-electron donor) has a conductivity, $\sigma = 1.47 \times 10^4$ S / cm at 66 K, a conductivity approaching that of metals (Cu at 298 K has $\sigma = 6 \times 10^5$ S/cm). Calvin and co-workers [15,16] have found that complexes of *o*-chloranil i.e., 3,4,5,6-tetrachloro 1,2-benzoquinone) with phthalocyanine and violanthrene show a large increase in electrical conductivity compared to the sum of the conductivities of the individual donors and acceptors. They have also detected photoconduction in thin films of these EDA complexes. A photovoltaic effect has been shown [17] with thin films containing porphyrene-*o*-chloranil EDA complexes and involvement of such complexes in storage and conversion of solar energy is a current field of research [18]. In the solid state the properties of EDA complexes cannot be completely explained by the simple Mulliken theory; a detailed analysis of solid state properties (like specific heat, magnetic properties etc) has been done theoretically by Soos and Klein [19].

Some studies of EDA complexes in micellar media have been reported [20-22]. Because of the intrinsic importance of such media themselves, these studies are of potential technological value.

In many nucleophilic and electrophilic substitution reactions, EDA complexes have been reported to act as intermediates. For example, the observed rate of the reaction between 2,4-dinitrochlorobenzene (N) and aniline (An) in ethanol medium has been explained [23] by assuming the following two paths:

$$\mathrm{N + An \rightarrow products}$$

$$\mathrm{N + An \rightleftharpoons N{\cdot}An \rightarrow products}$$

Here, owing to the presence of strongly electron-withdrawing nitro groups, N is an electron acceptor while aniline is a known electron donor and the assumption of the EDA intermediate (N·An) is quite plausible. The rate of acetolysis of 2,4,7-trinitro-9-fluorenyl-*p*-toluene sulphonate (an electron acceptor) has been shown to be enhanced [24] by π-electron donors like hexamethylbenzene, phenanthrene and anthracene; the observed catalysis in this case has been interpreted in terms of EDA complex formation between the π-donors and the trinitrofluorene derivative in the activated state rather than in the ground state. Detailed discussion about EDA complexes occurring as reaction intermediates may be found in references [25-39].

Recently [40] a simple, portable sensor device has been fabricated for detection of mustard gas (HD) analogues on the basis of CT complex formation between Cu(II) acetate and HD. The study of EDA complexation is currently gaining importance for understanding photosynthesis [41], electron transfer across DNA strands [42,43] and fullerene CT complexes [44,45].

Electron donor-acceptor complexes possibly have some role in drug-receptor binding. Doxycycline hydrochloride forms a charge transfer complex [46] with riboflavin (**Figure 1**) in aqueous and aqueous-ethanol media, which are close to biological systems. Temperature and dielectric constant of the medium have pronounced effect on the formation constant of the complex. Since change in body temperature also changes the dielectric constant of the body fluid, the results obtained in the present work may have some relevance in physical pharmacy. Moreover, the ionization potential of the drug doxycycline hydrochloride and electron affinity of riboflavin may be utilized in theoretical modeling of mechanism of drug action. It has further been established that the free base form of the drug actually binds to the riboflavin molecule.

A spectrophotometric study [47] shows that the drug molecule 4-acetamidophenol i.e., paracetamol (donor) forms 2:1 molecular complexes of electron donor-acceptor type with a series of quinines (acceptors) of which one is the biologically important molecule, menadione (vitamin K_3). Most of the molecular complexes found in literature [1-3] have stoichiometry 1:1 in solution, though in the solid state a good number of 1:2 complexes are known to exist. Formation of charge transfer complex of 2,3-dichloro-1,4-naothoquinone with 4-acetamidophenol in pure ethanol and aqueous-ethanol media are close to biological systems. Hence such work also may be of some relevance in physical pharmacy.

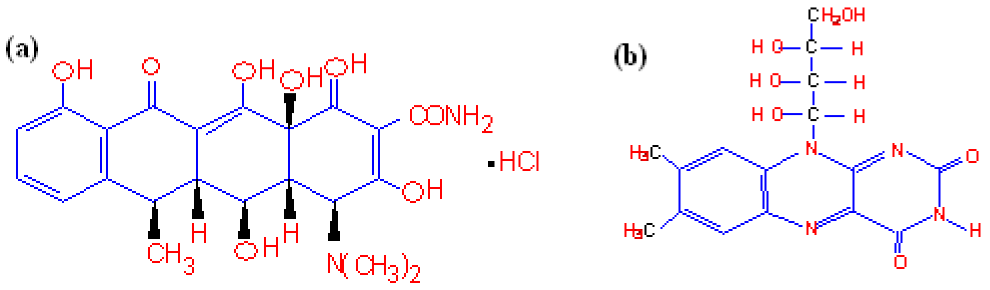

Figure 1 (a) Doxycycline hydrochloride (b) Riboflavin

The CT complex formation of [60]- and [70]fullerenes with retinol palmitate (vitamin A oil) may be used to solubilize the fullerenes in vitamin A oil [48] as solvent and this solution may be of pharmaceutical utility in testing the biological activity of the fullerenes *in vivo.*

Host-guest or inclusion complexes

Molecules having cavities where other molecules or ions can be held by non–covalent bonds (mainly, van der Waals forces and hydrogen bonding) form a novel class of materials known as 'hosts', cyclodextrins form the first of this type. They are cyclic oligosaccharides containing a minimum of six D(+) glucopyranose units attached by α-1,4 linkages which was established by Freudenberg *et. al.* [49] Cyclodextrins are produced by the action of *Bacillus macerans* amylase on starch. The natural α, β and γ-cyclodextrins (α-CD, β-CD and γ-CD) consist of 6,7 and 8 units of glucose respectively. Their ability to form inclusion complexes in aqueous solution is due to the typical arrangement of glucose units as shown in **Figure 2**.

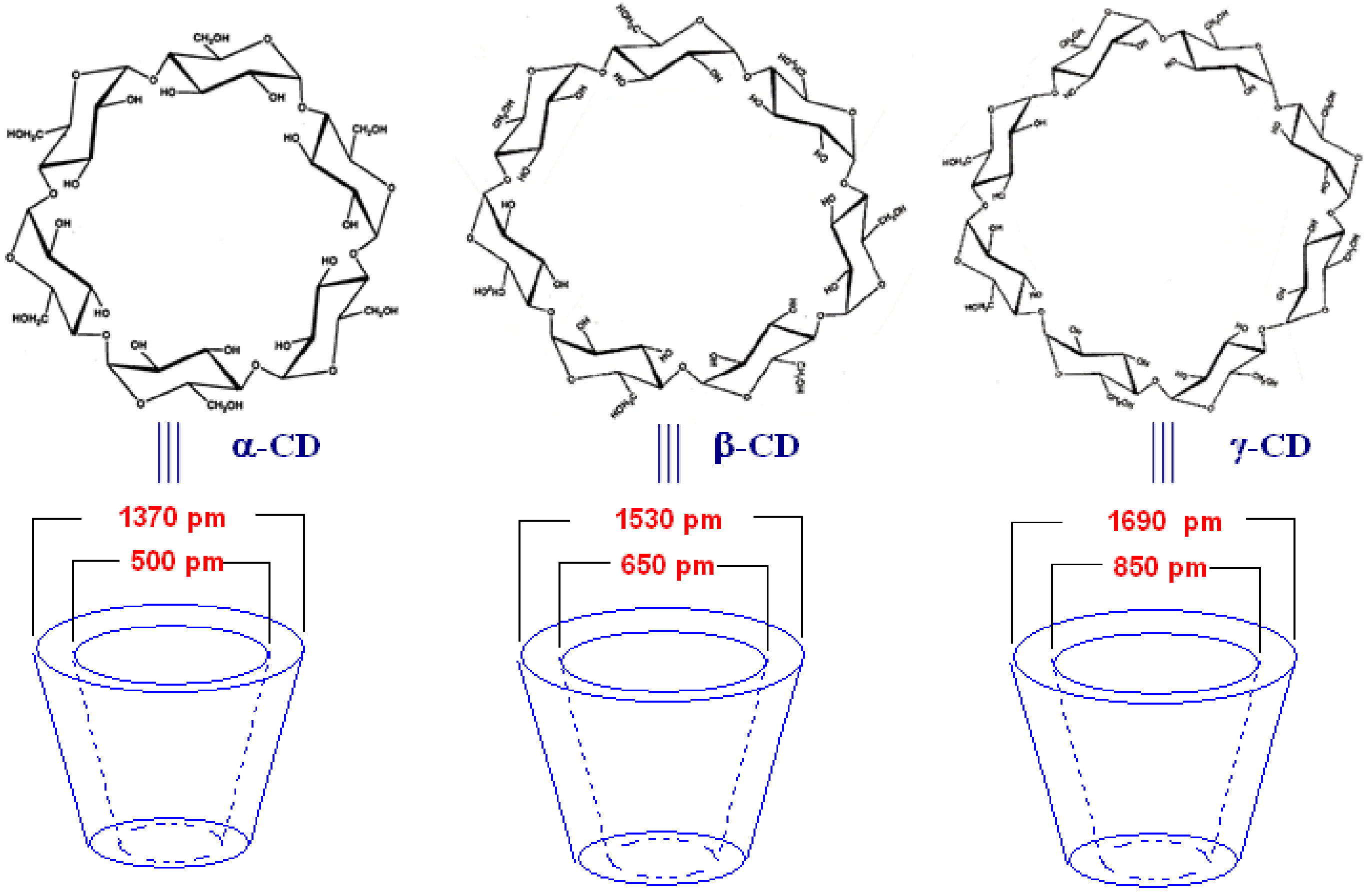

Figure 2 Cyclodextrins and their conical conformations

Although an isolated cyclodextrin molecule looks like a torus (or doughnut ring), the molecule in aqueous solution assumes a truncated conformation [50,51] due to hydrogen bonding of the –OH groups with water. In such conical conformation the cone-height is about 800 pm and the inner diameter of the cavity is between 500 and 850 pm (Figure 2). A fascinating property of the cyclodextrins is their ability to incorporate other organic compounds into their cavity, both in the solid state and in solution. This was first recognized by Freudenberg and later substantiated through complexation studies by Cramer, Saenger and others [52-55]. Owing to the non-toxicity of cyclodextrins, their ability to form inclusion complex has very important pharmaceutical application. For example, an important drug molecule included [56] in γ-CD is Mytomycin C, the inclusion complex being shown in **Figure 3**. The aziridine ring (**Figure 4**) of Mytomycin C being well within the hydrophobic cavity of γ-CD, is protected from degradation in acidic solution [57].

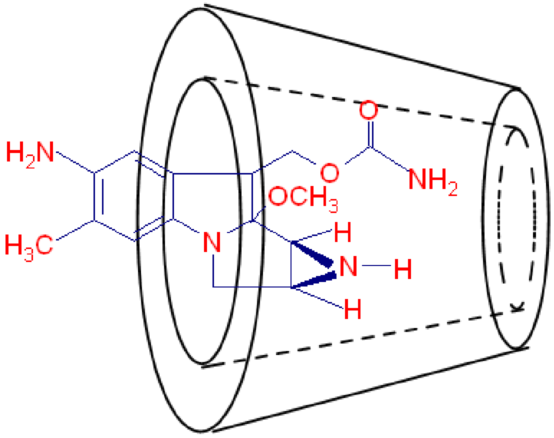

Figure 3 Mytomycin C included in γ-CD

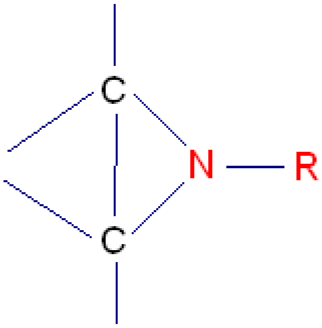

Figure 4 Aziridine ring

Cyclodextrins are studied as solubilizing and stabilizing agents in pharmaceutical dosage forms. Lach *et. al.* [58,59] used the complexing ability of cyclodextrins to trap, stabilize and solubilize sulphonamides, tetracyclines, morphins, aspirin, benzocaine, ephedrine, reserpin and testoterone. The aqueous solubility of retionic (0.5 mg dm^{-3}), a drug used topically in the treatment of acne [60], is increased to 160 mg.dm^{-3} by complexation with β-CD. Dissolution rate plays an important role in bio-availability of drugs, fast dissolution usually favouring absorption. Thus, the dissolution rate of famotidine [61], a potent drug in the treatment of gastric and duodenal ulcer and tolbutamide, an oral antidiabetic drug, are both increased by complexation with β-CD [62]. If some –OH groups are alkylated, the resulting cyclodextrin has been reported to be useful in sustained drug release. Thus, ethylated β-CD has been used [63] to retard, through inclusion complex formation, the delivery of isosorbide dinitrate, a vasodilator.

The second generation of hosts is the series of crown ethers and cryptands [64-67]. Approximately 5000 different crown compounds are now known [68]. Structures of some crown ether molecules are shown in **Figure 5**. Crown ethers have received much attention in both chemistry and biology [69,70]. They act antiulcerogenically against histamine induced ulcers [71] and as antibacterial agents [72]. Chiral recognition through host-guest complexation with crown ethers as hosts is a subject of very recent activity [73,74]. Thus, molecular recognition of tryptophan enantiomers in aqueous medium has been recently attempted through the synthesis of crown ether-tethered cyclodextrin hosts [75]. Crown ethers are also being used in the synthesis of rotaxanes whose the precursors are often host-guest complexes [76,77]. In particular, dibenzo-24-crown-8 ethers have recently been used [78] for the synthesis of [3] rotaxanes. In a recent work [79] vertical ionisation potentials of a number of crown ethers from CT bands of their molecular complexes have been reported. Crown ethers also play an important role in surfactant [80] action and also in molecular semiconductivity [81]. They can provide a suitable model for studying transport of ions through membranes [82] and membrane separation processes [83]. Research on crown ethers has been motivated by their remarkable ability to complex alkali and alkaline earth metals [84]. A crown ether with a large cavity can accommodate two cations simultaneously as exemplified by the disodium salt of the 30-membered crown ether, dibenzo-30-crown-10. The most important features of such cyclic polyether molecules which determine their binding strength are: number and types of donor atoms, dimension of the cavity, presence of substituents on the donor ring and degree of ligand preorganisation [85]. Thus crown ethers can be treated as suitable hosts for a wide variety of ions/molecules.

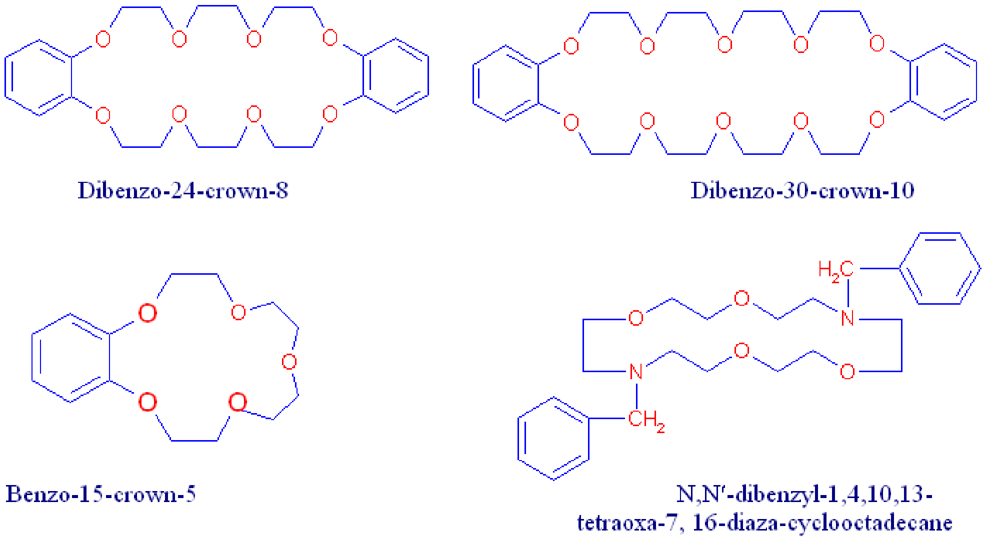

Figure 5 Structures of different Crown ethers (host molecules)

The calix[n]arenes appeared as the third generation host compounds after cyclodextrins and crown ethers. The first calixarene was synthesised by Gutsche [86]. Calixarenes made up of phenol and methylene units have many conformational isomers because of two possible rotational modes of the phenol units: the oxygen-through-the-annulus rotation and the para-substituent-through-the-annulus rotation. The conformational isomers thus yield a great number of unique molecular cavities with different size and shape. Some widely used calixarene molecules are shown in **Figure 6**.

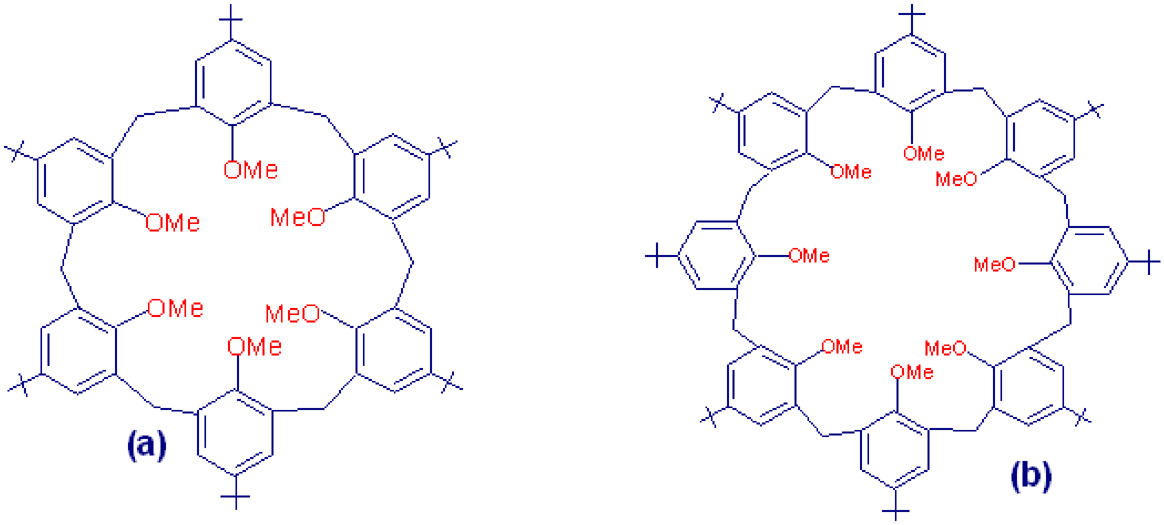

Figure 6 (a) 37,38,39,40,41,42-hexa-methoxy-5,11,17,23,29,35-hexa(4-tert-butyl) calyx[6]arene, (b) 49,50,51,52,53,54,55,56-octamethoxy-5,11,17, 23,29,35,41,47-octa(4-*tert*-butyl)calix[8]arene

When a molecule or ion is incorporated in the cavity of a host molecule, the former is called ‘guest’ and the molecular adduct is called an ‘inclusion’ or a ‘host-guest’ complex and study of such complexes is an important aspect of what is now being called ‘supramolecular chemistry’ [12]. Some well studied guest molecules / ions are Na^+, K^+, enzyme, etc (**Figure 7**). The studies of selective alkali cations binding with designed alkali cryptands are the field of molecular recognition.

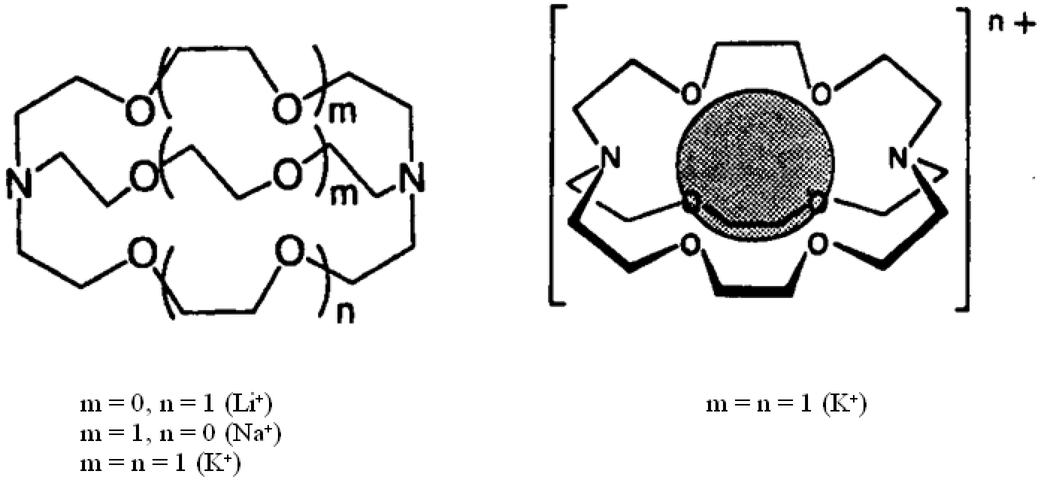

Figure 7 The pronounced selectivity of size complimentarity between cation and intramolecular cavity of the cryptand.

A primary criterion for inclusion of a guest molecules or ion within the host's cavity is obviously their relative size (i.e., size selectivity). Thus host–guest complexation is based, depending on the solvent and the type of host and guest, on a combination of several intermolecular interactions as listed below:

(a) Steric fit, (b) van der Waals interaction such as dispersive forces, dipole-dipole and dipole-induced dipole interactions, (c) electrostatic interaction, (d) hydrogen bonding and (e) charge transfer interaction.

Sometimes a guest molecule may be incorporated within the cavity formed by an assembly of molecules, which individually do not have cavity. An example is given in the following section.

Fullerenes as guests in inclusion complexes

The unique physical and chemical properties of [60]- and [70]fullerenes [87,88], viz., electronic absorption band expanding throughout the entire UV-Vis spectrum [89-91], efficient singlet oxygen sensitising ability [92-94], strong electron acceptor character [95,96] and superconductivity [97] upon doping with alkali metals, make them an attractive component to be incorporated in functional molecular assemblies and supramolecular arrays. The first example of fullerene involved in supramolecular phenomena was reported by Ermer [98] in 1991. In this work hydroquinone (HQ) and [60]fullerene were dissolved in hot benzene-in a 3:1 (HQ: [60]fullerene) molar ratio and the solvent was allowed to evaporate giving rise to black crystals. On X-ray crystallographic analysis it was found that in these crystals a [60]fullerene ball was incorporated within the cage formed by hydrogen bonded HQ molecules. Another such example, where [60]fullerene is incorporated as a guest molecule in crystal lattice is the partial charge transfer solid, $C_{60}.\{(\eta^5\text{-}C_5H_5)_2Fe\}_2$ whose crystal packing [99] is shown in **Figure 8**.

The redox potential of ferrocene is not sufficient to form C_{60}^{-} anion. When ferrocene solution in benzene is mixed with that of [60]fullerene in the same solution, co-crystallization results to form the aforementioned solid. One of the (electron-rich) cyclopentadienyl rings of ferrocene is in slightly offset π-contact with one of the (electron poor) pentagonal rings of [60]fullerene. The inter-planar distance (3.3 Å), similar to that between planes of graphite, is typical of that between neutral species, rather than between ions, so that full electron transfer does not occur in this case. Many more supramolecular incorporation of fullerenes in molecules with cavity have by now been reported [6-8].

In an attempt to increase the water solubility of [60]- and [70]fullerene, which can be of great importance for potential biological applications [100,101], it was discovered [102] that boiling aqueous solution of γ-CD, but not β-CD, was able to extract [60]fullerene from a mixture of [60]- and [70]fullerene. A host-guest complex with 2:1 (γ-CD:C_{60}) stoichiometry was proposed to be responsible for the selective extraction of [60]fullerene. The complex has a bicapped structure (**Figure 9**) which has been supported by ^{1}H and ^{13}C NMR and fast atom bombardment (FAB) mass spectrometric studies as well as by elemental analysis [103]. Further evidences for the formation of (γ-CD)$_2$.C$_{60}$ host-guest complex were provided in some subsequent work [104].

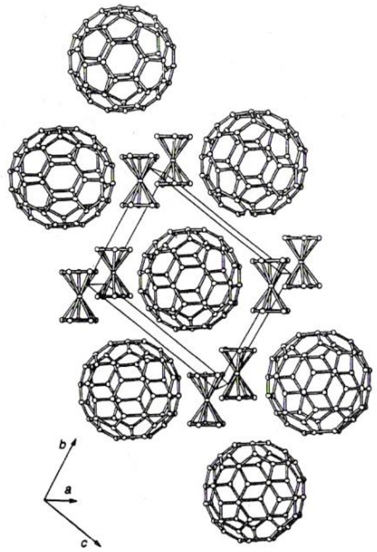

Figure 8 A view [99] of the packing in $C_{60}.\{(\eta^5\text{-}C_5H_5)_2Fe\}_2$

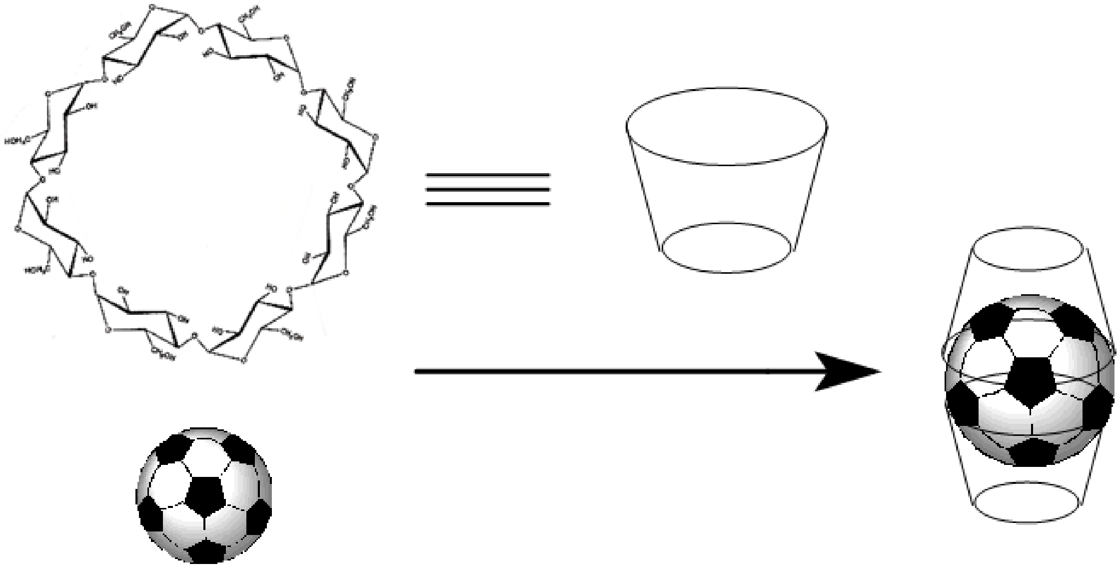

Figure 9 Bicapped structure of [60]fullerene.(γ-CD)$_2$ host-guest complex

Another macrocyclic compound which has been studied [105] with regard to its ability to form inclusion complexes with [60]fullerene is cyclotriveratrylene (CTV). The X-ray structure shows that [60]fullerene adopts a nesting position at van der Waals contact distance above the concave structure of the CTV macrocycle (**Figure 10**). Again it can be assumed that a weak π-π donor-acceptor interactions are contributing to the complex formation.

The complexation between calix[n]arenes [106-109] and fullerenes [87,88] evoked a new dimension in host-guest chemistry. Calix[n]arenes not only have well-ordered macrocyclic arrays of aromatic rings but also possess the necessary flexibility which allows docking of large guest molecules such as fullerenes. The groups of Atwood [4] and Shinkai [110] discovered independently that toluene solutions of [60]fullerene and *p*-Bu^t-calix[8]arene (**1**) form a sparingly soluble clathrate in 1:1 stoichiometry and the method was excellently utilised for the separation of the components from a mixture of [60]- and [70]fullerenes.

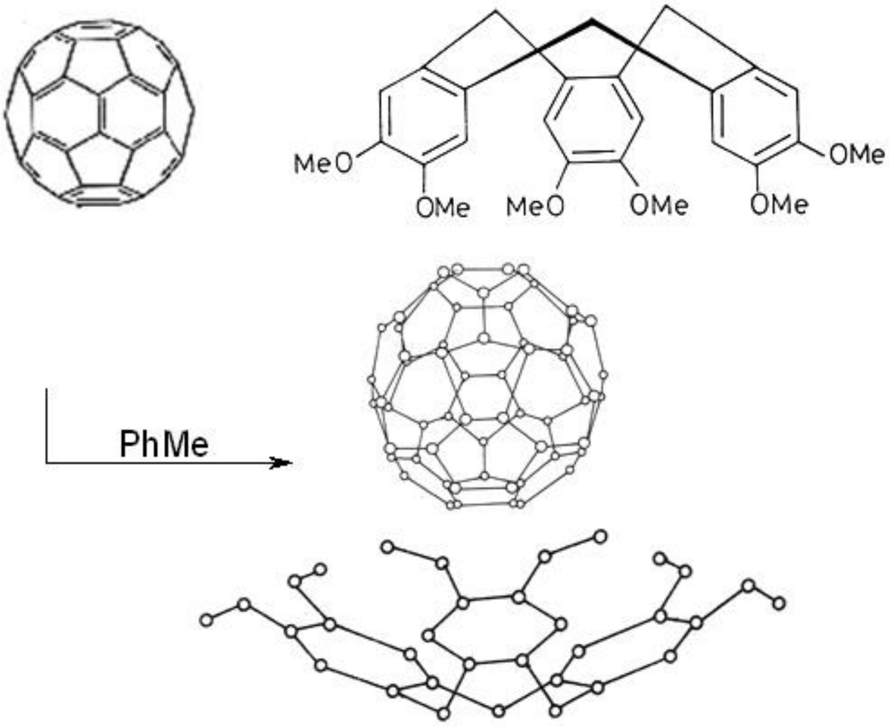

Figure 10 Ball and stick representation [105] of the X-ray structure of the [CTV][60]fullerene complex

In this clathrate, the fullerene most likely resides within the cavity of the macrocycle, presenting a structure, which resembles that of a ‘ball and socket’. Verhoeven and co-workers [111] carried out solid state ^{13}C NMR spectroscopic investigations to explore the nature of the intermolecular interactions in the complex between *p*-Bu^t-calix[8]arene and [60]fullerene. Solid state complexes of calix[6]arene with [60]- and [70]fullerenes have also been reported [112] by Atwood *et. al.*. Fukuzawa and co-workers [113] have reported comprehensive investigations of the complexation between calix[n]arene and [60]fullerene in organic solvents. Recently calix[n]arenes of suitable size and rim substituents are being designed and synthesised for developing methods of separation of a desired fullerene from carbon soots containing fullerne mixtures by utilising the phenomenon of preferential encapsulation of one fullerene over the other. For example, Komatsu has very recently [114] reported the synthesis of homooxacalix[n]arenes; in this work preferential precipitation of [70]fullerene from a mixture of toluene solutions of [60]- and [70]fullerenes was accomplished with *p*-trihalohomooxacalix[3]arenes prepared by the reductive coupling of diformyl phenols. It has further been reported that heavy halogens (Br and/or I) are essential at the para position of the trihalohomocalix[3]arene for obtaining good yields and selectivities.

Dibenzo 24-crown-8 forms inclusion complex [115] with [60]fullerene but the formation constant of the dicyclohexano 24-crown-8 - [60]fullerene complex is much lower in magnitude characteristic of non-inclusion type of molecular adducts [116]. This shows that replacement of benzene ring by cyclohexane decreases the inclusion capacity of the crown ether. Since the cyclohexane ring has much higher conformational flexibility than the benzene ring, it probably decreases the cavity size of the crown ether and thus makes it unable to include the fullerene balls. It is observed (Figure 8) that at any temperature the formation constant of the [60]fullerene complex is higher than that of the [70]fullerene complex although [70]fullerene is known [117] to have higher electron affinity than [60]fullerene. This shows that it is not always possible to explain the order of *K* values of non-inclusion type of CT complexes only in terms of electron affinities of the concerned acceptors probably because their formation involves many energy terms (in particular, solvation).

The resorcin[4]arene (2,8,14,20-tetrapentadecylpentacyclo [19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25), 3, 5, 7 (28), 9, 11, 13 (27), 15, 17, 19 (26), 21, 23- dodecaene-4,6,10,12,16,18,22,24-octol) (shown in **Figure 11**) acts as an electron donor with vertical ionization potential of 7.62 eV and also as a host for [60]fullerene guest [118]. It therefore has ability to include [60]fullerene ($K = 8 \times 10^4$ mol^{-1}dm^3 at 25^{0}C) in preference to [70]fullerene ($K = 7 \times 10^2$ mol^{-1}dm^3 at 25^{0}C), a fact which may possibly be utilized in purification of [60]fullerene from carbon soot.

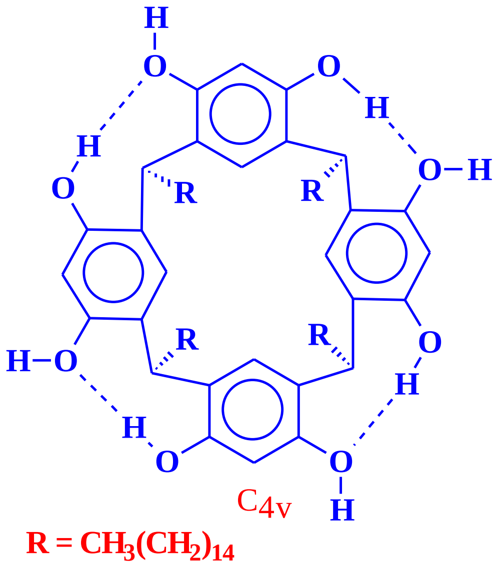

Figure 11 2,8,14,20-tetrapentadecylpentacyclo $[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]$octacosa-1(25), 3, 5, 7 (28), 9, 11, 13 (27), 15, 17, 19 (26), 21, 23- dodecaene-4,6,10,12,16,18,22,24-octol

Tribenzotriquinacene receptor (**R**) leads exclusively to the formation of 1:1 complexes [119-121] with C_{60} (shown in **Figure 12**). The resulting huge K_1 value of 14,550 M−1 for the association constant of $C_{60} \subset$ **R** confirms [122] the optimized shape complementarity between the receptor **R** and its C_{60} guest as a result of an increasing number of aromatic rings appropriately positioned at the upper rim of the half-spherical shaped receptor **R**. The functionalized upper rim of host **R** prevents the formation of a 1:2 complex. Both the suppression for binding of a second receptor (i.e. formation of a 2:1 host–guest complex) as well as the increase of complex stability of the 1 : 1 complex can be rationalized in terms of multiple additive van der Waals and π–π interactions between C_{60} and the aromatic groups of the receptor, as revealed by DFT+D and force-field calculations. Combining results from spectroscopic and theoretical investigations leads to predictions in light of future receptor designs, which – apart from shape complementarity – will have to consider an optimized electronic match (i.e. partial charge transfer) between the receptor and the fullerene host.

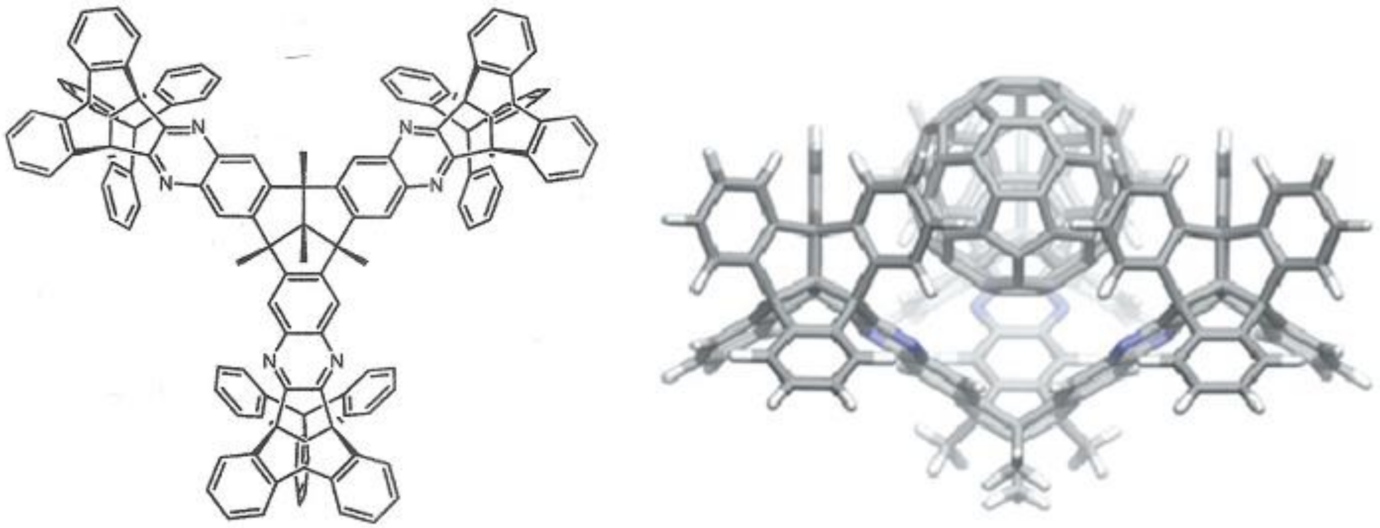

Figure 12 Tribenzotriquinacene and Force field optimized structures [122] of the 1 : 1 C_{60} complexes of R

Recently, the structure and stability of the inclusion complex formed by the fullerene C_{60} and the cucurbituril CB[9] is shown by DFT, semi-empirical and classical molecular dynamics methods. This results indicate a high structural compatibility between the two monomers, which is evident from the potential energy curve for the inclusion process of the C_{60} into the CB[9] cavity. The interaction between the two monomers is mainly of the van der Waals type and leads to a highly stable complex. Thermal contributions and environmental interaction are taken into account by the free energy of binding of -224 kJ mol^{-1}, indicating that even in aqueous medium the complex remains very stable. It is known that cucurbiturils with odd n (CB[5] and CB[7]) are water-soluble, while those with even n (CB[6], CB[8] and CB[10]) are not [123,124]. The reasons for this are not well understood.

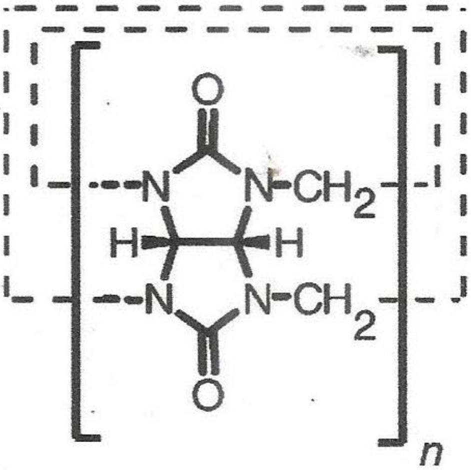

Figure 13 Cucurbit[n]uril[124], CB[n]

Based on the robust photo-responsive property [125] of the azobenzene structural unit (**Figure 14**), a novel photo-responsive nanoring host molecule ([4]AB) composed by four azobenzene groups was designed. By means of quantum chemical methods, the host–guest interactions between the designed nanoring host and fullerenes C_{60} as well as C_{70} were investigated. It is revealed that the designed host [4]AB is almost circular with an aspect ratio of ca. 1.01 and a diameter of 13.38 A, with a shape and size that is excellent for the encapsulation of C_{60} or C_{70} fullerenes. The high binding energies suggest that both $[4]AB\supset C_{60}$ and $[4]AB\supset C_{70}$ are stable host–guest complexes, and the guest C70 is more strongly encapsulated than C60 in the gas phase. The thermodynamic information indicates that the formations of the host–guest complexes are thermodynamically spontaneous, so host–guest recognition between [4]AB and fullerene C60 and C70 is very favorable. Inferred from the UV-vis- NIR spectroscopy, together with the robust photo-responsive properties of azobenzene group, the guest C60 and C70 could be released facilely from the cavity of the host [4]AB via configuration transformation from the trans- to the cis-form of the host under 474 and 506 nm photo-irradiation, respectively.

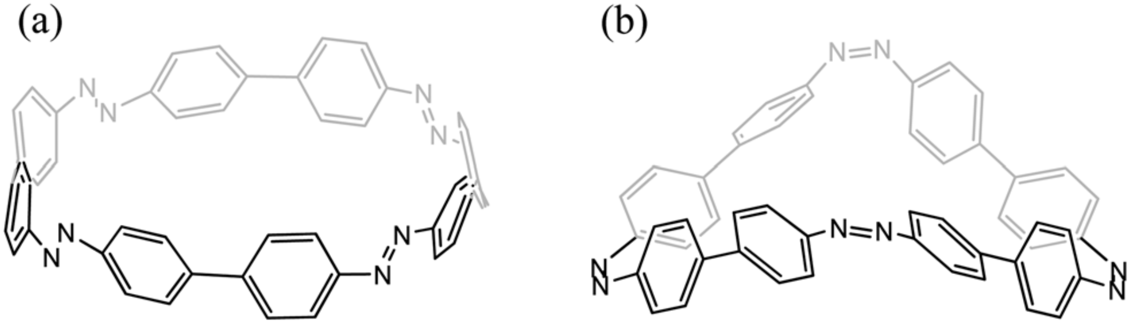

Figure 14 The optimized chemical structures [125] of the [4]AB host in the (a) trans-form and (b) cis-form (H atoms are omitted for clarity).

On reflection, such theoretical complementary host–guest chemistry will be useful for the future possible experimental study of systems with the properties of reversible and facile catching and release of fullerene guests. Moreover, we also anticipate that further experimental syntheses of the present designed host [4]AB, or analogous functional molecules, will provide a practical base for the development of novel photo-responsive hosts in chemical, materials and even biological systems.

Polymer composites of fullerenes

Poly(benzyl ether) dendrimer **1** has at its centre a cyclic dimer of porphyrin (**Figure 15**) [126]. This dendritic host can incorporate fullerenes into the cavity of its core unit and solubilize them in a variety of solvents, depending on the solubility of the dendritic wedges. Furthermore, thanks to the high compatibility of poly(benzyl ether) dendrimers with commodity polymers, dendritic host **1** allows a highly stable, molecular-level dispersion of fullerenes in, e.g., poly(methyl methacrylate), affording a homogeneous composite film.

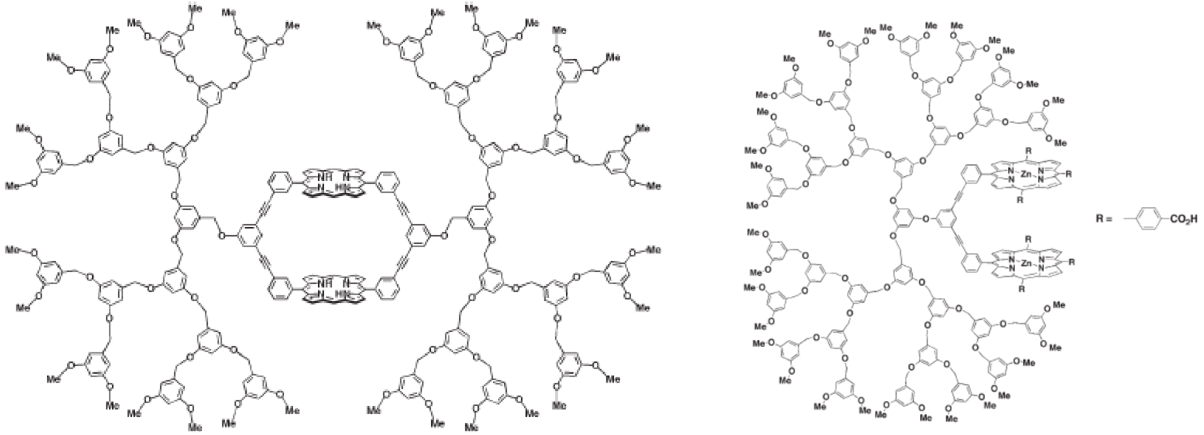

Figure 15 Schematic molecular structure of host 1 with poly(benzyl ether) dendritic wedges and has carboxylic acid functionalities for self-assembly [126].

Molecular Aggregates

The most widely known molecular aggregates are ‘association colloids’ formed by surfactants. Presently such aggregates are being called ‘micelles’ and ‘inverted micelles’ (shown in **Figure 16**). Micelles are formed when the continuous medium is water and the polar head groups of the surfactant molecules/ions in the aggregate are exposed to water. When the continuous medium is oil (i.e., an organic liquid which is immiscible with water at ordinary temperature), the polar head groups of the surfactant are within the aggregate and the non-polar tails are exposed to the bulk (oil), the aggregate is called ‘reverse micelle’.

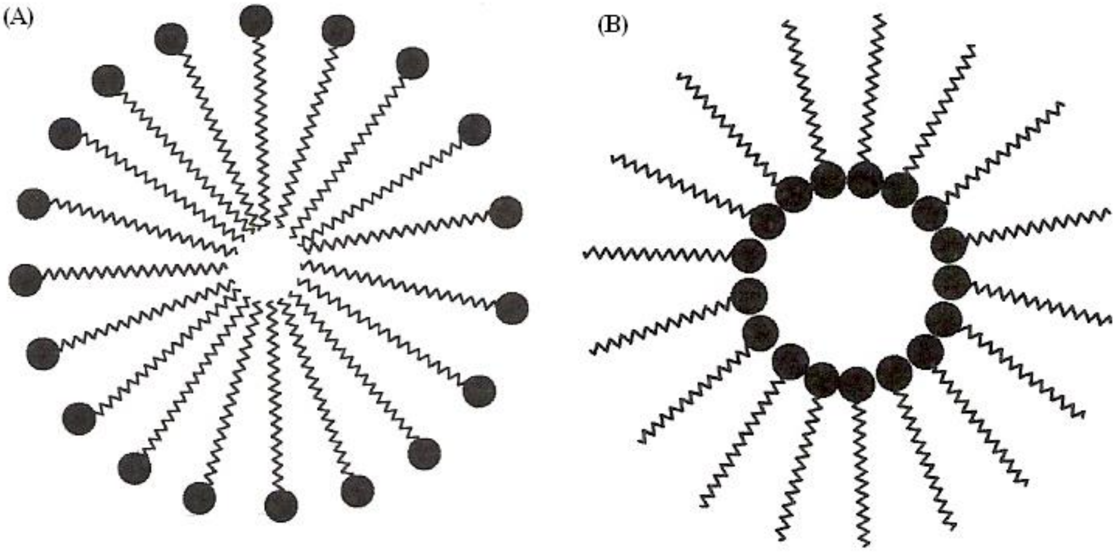

Figure 16 (A) Assembly of surfactant molecules in aqueous medium, micelle (B) Assembly of surfactant molecules in non-aqueous medium, reverse micelle

The molecular architecture of all these surfactants is similar: they have a polar (‘head’) group on one end and a non-polar long hydrocarbon chain (‘tail’) on the other. Formation of both of these types of aggregates results from a tendency of the non-polar chain to avoid water molecules and of the polar head groups to remain as much exposed to water as possible; for each case, aggregation starts only above a certain concentration known as critical micellisation concentration (cmc) which is different for different surfactants. Thermodynamic aspects of such micellar media and some spectroscopic studies in such media have been reported in references [20-22, 127-131]. Some typical surfactant molecules are listed in **Table 1**.

Table 1 Names, structures and micellar parameters of some aqueous normal micelle-forming surfactants

Surfactant	CMC (mM)	Aggregation number
Hexadecylpyridinium chloride, CPC [$C_{16}H_{33}N^+C_5H_4Cl^-$]	0.9	95
Hexadecyltrimethylammonium bromide, TAB [$C_{16}H_{33}N^+(CH_3)_3Br^-$]	0.4-0.9	61
Sodium dodecylsulphate, SDS [$C_{12}H_{25}SO_4^-Na^+$]	8.1	62
Sodium hexanoate, NaH [$C_5H_{11}CO_2^-Na^+$]	900.0	—
Polyoxyethylene(23)dodecanol, Brij-35[$C_{12}H_{25}(OCH_2CH_2)_{23}OH$]	0.1	40
Polyoxyethylene(15)nonylphenol, Igepal CO-730 [$C_9H_{19}C_6H_4O(CH_2CH_2O)_{15}H$]	0.28	52

Besides these, both [60]- and [70]fullerene have been reported to form aggregates under three conditions: (i) when the fullerene vapour is quenched in an inert gas atmosphere [132-136] (ii) when kept for a long time in aromatic solvents [137-142] such as benzene and *o*-xylene and (ii) when sonicated in polar solvents like acetonitrile and benzonitrile [143-145].

By UV-vis absorption and fluorescence spectroscopy it has been established that 25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**1**) forms reverse micelles in CCl_4 and *n*-hexane media. The new feature of this compound as a surfactant is that even before micelle formation it can incorporate water molecules and the critical micellization concentration (cmc) in nonaqueous media increases with increase in ω (=water:**1** mole ratio). At concentrations above cmc, the calixarene **1** forms with [60]fullerene a host-guest complex of 1:2 stoichiometry which may be modeled (**Figure 17**) as a bi-capped complex resulting resulting from close proximity of the reverse micellar aggregates. 1H NMR spectrometric determination of the formation constant (*K*) of the inclusion complex of [60]fullerene with **1** in CCl_4 has revealed that *K* increases [146] on addition of microquantities of water. This has been rationalized by assuming that the -OH groups of the calix[4]arene molecules attach themselves to the water micropool of the reverse micelles by forming H-bonds and the individual calix[4]arene molecule obtains a conical conformation with a wider rim diameter than that in the absence of water and that this preorganization facilitates inclusion. By utilizing the spectral variation of the [60]fullerene. **1** complex in CCl_4 as the continuous medium with change in ω, a critical ω (=8) has been found below which the water in the micropool is “bound” and above which “free” water begins to accumulate in the water micropool [60]fullerene is known to aggregate [147, 148] in water and all experimental and theoretical evidences support that the aggregates contain $(C_{60})_{13}$ units. By simple kinetic study of the aggregation process and scanning electron microscopy (SEM) it is found that when methanol is added to a solution of [60]fullerene in CCl_4, spontaneous aggregation starts immediately and the aggregation numbers (*n)* found to be dependent on the CCl_4:CH_3OH ratio (v/v*)* of the medium. One particular ratio of the two liquids gives uniformly sized $(C_{60})_{13}$ clusters for about 10 min. The values of *n* correspond to the minima of the previously reported energy calculations and in the present work, they have been shown to be a natural consequence of stacking of cuboctahedra made up of C_{60} molecules (**Figure 18**). A Young diagramlike method has been developed for counting the number of C_{60} molecules in these cuboctahedral stacks and the numbers obtained from this model and also from the present chemical kinetic and SEM studies agree very well with the “magic numbers” obtained by mass spectrometric studies.

Supramolecular peapods

Supramolecular peapods Compound (**Figure 19**) is another type of dendritic host, bearing at its focal core an acyclic dimer of a zinc porphyrin [149]. This dendritic molecule coassembles with fullerenes such as C_{60} and C_{70} to form an interesting low-dimensional nanostructure referred to as a ‘supramolecular peapod’, where included fullerenes are aligned within a dendrimer-coated supramolecular porphyrin nanotube. Peapod-like fullerene-included carbon nanotubes (Figure 19) have attracted attention due to their unique electronic properties that arise from hybridization of carbon nanotube p-electrons with those of the inner fullerenes [150]. The zinc porphyrin dimer, at the focal core of compound, is acyclic and may not be suitable for the incorporation of fullerenes. However, because of the presence of carboxylic acid groups, this acyclic core, upon interaction with fullerenes, undergoes a guest-directed cyclodimerization via intermolecular hydrogen-bonding interactions. The fullerene-included supramolecular dimer, thus formed, is further assembled bilaterally via hydrogen-bonding interactions of the residual carboxylic acid groups, to accomplish the peapod structure. According to TEM analysis, the resulting low-dimensional nanostructure is several micrometres long and possesses a uniform diameter of 15 nm, in agreement with a prediction from the CPK model (12 nm). Without fullerenes, supramolecular dimer only forms an irregular hydrogen-bonded aggregate due to conformational freedom in the acyclic core. At -40^{0}C included C_{60} within the porphyrin nanotube shows a broad ^{13}C NMR signal at δ 139.6 ppm in 1,1,2,2-tetrachloroethane-*d*2, indicating highly constrained motion of C_{60} in the tubular space.

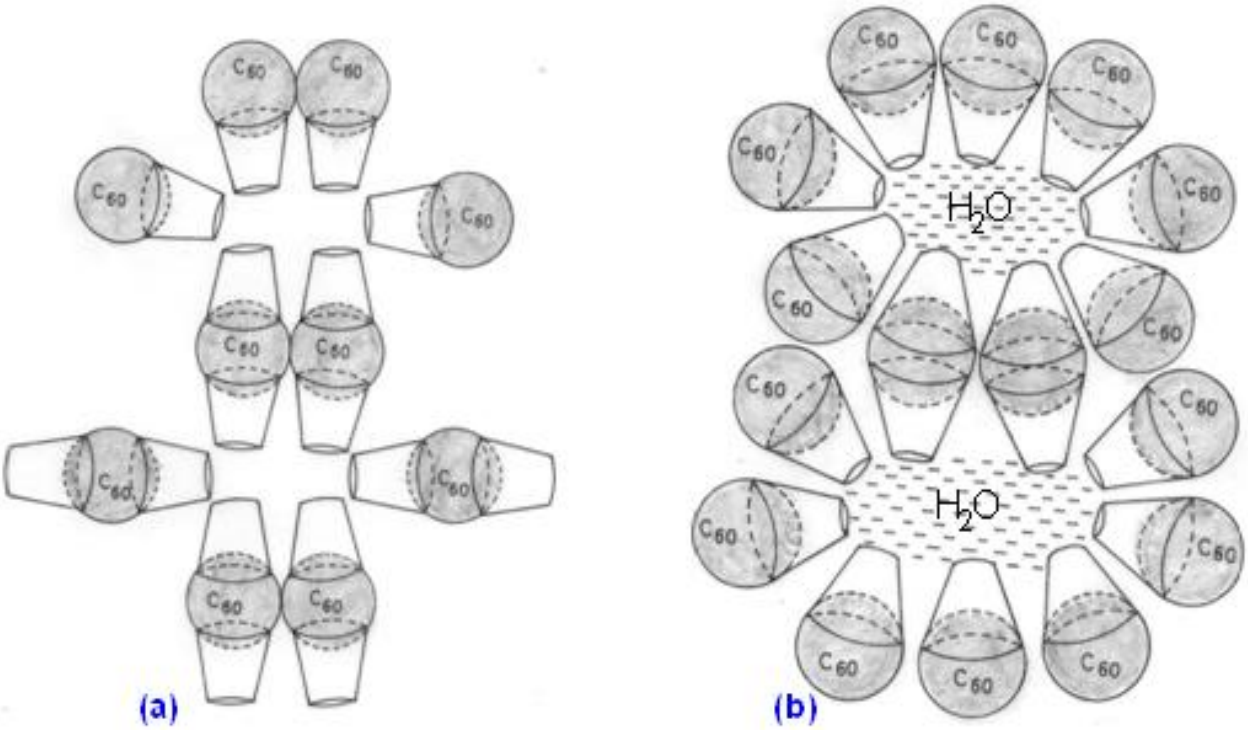

Figure 17 A model for reverse micelles of calixarene **1** helping 1:2 complex formation (a) in absence of water and (b) in presence of water

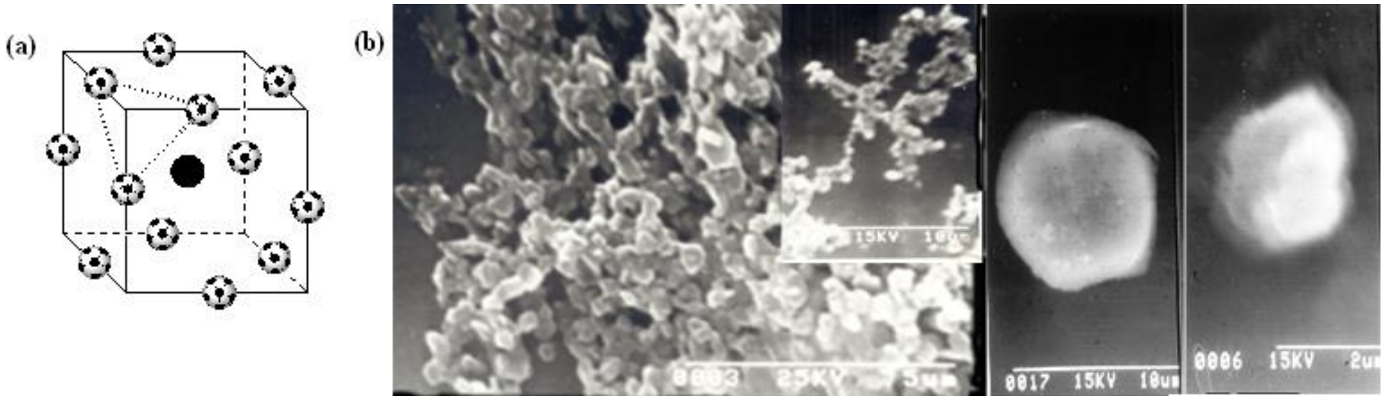

Figure 18 (a) $(C_{60})_{13}$ cuboctahedron, (b) SEM figures of two large clusters and two fractal designs

Figure 19 Schematic Representation [149] of C_{60} included carbon nanotube

Conclusions

Supramolecules host–guest chemistry have bio-physical importance. Inclusion complex of drug with selective cavitant use in drug delivery system. Selective metal ions can be extracted using cavitant having proper diameter for inclusion complex. Fullerene can also be extracted from mixture of fullerene or carbon soot using this method. Host-guest complexation with cavitands according their structure and properties may be helpful for material chemistry application in the future. [60]fullerene aggregates in water and all experimental and theoretical evidences support that the aggregates contain $(C_{60})_{13}$ units. Minima of the energy calculations and the other reported work, it has been shown to be a natural consequence of stacking of cuboctahedra (symmetry based approached) made up of C_{60} molecules.

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