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Mini Review

Cucurbiturils – a New Family of Host Molecules

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Abstract

The supramolecular chemistry of cucurbituril, a synthetic receptor, is fascinating because of the remarkable guest binding behavior of the host. Although cucurbituril is potentially as useful as crown ethers, cyclodextrins, and calixarenes in many applications, its chemistry has not been developed much until recently because of several shortcomings. Recently we synthesized cucurbituril homologues and derivatives. These new members of the cucurbituril family have expanded the scope further, and interest in them has grown enormously. The diversity in guest binding behavior has led to many interesting studies such as redox control of guest binding, stabilization of charge-transfer complexes inside the host cavity, encapsulation of drug molecules, formation of redox-controllable vesicles, and so on. The cucurbituril homologues and derivatives thus provide new opportunities in many areas of supramolecular chemistry including recognition, catalysis, separation, transport, and many others.

Introduction

Cucurbit[6]uril (CB[6]) is a hexameric macropolycyclic compound synthesized from an acid-catalyzed condensation reaction of glycoluril and formaldehyde. Although its synthesis was first reported in 1905 [1], its chemical nature and structure were unknown before the full characterization was reported by Mock [2]. The pumpkin-shaped molecule CB[6] has a cavity of ~5.5 Å diameter, accessible from the exterior by two carbonyl-laced portals of ~4 Å diameter. Although it resembles α-cyclodextrin (α-CD) in terms of cavity size, the highly symmetrical structure with two identical openings distinguishes it from α-CD. The host–guest chemistry of CB[6] has been studied extensively by Mock [3]. In a similar way to CDs, the hydrophobic interior of CB[6] provides a potential site for inclusion of hydrocarbon molecules. Unlike CDs, however, it forms stable inclusion complexes with various protonated alkyl- and arylamines.

The rigid structure and capability of forming stable complexes with molecules and ions also make CB[6] attractive as a building block for supramolecular assemblies. Over the last decade we synthesized a wide variety of mechanically interlocked molecules such as rotaxanes [4], polyrotaxanes [5], molecular necklaces [6], rotaxane dendrimers [7] and rotaxane-based molecular switches [8] using CB[6] as a molecular bead. We also carried out DNA binding studies of pseudorotaxanes comprising CB[6] and polyamines [9] and investigated the potential utility of rotaxane dendrimers as gene transfer vectors [10]. Our work in this area has been summarized in recent review articles [11, 12]. In addition, several other applications of CB[6] have been demonstrated. For example, CB[6] can facilitate chemical reactions with large rate acceleration inside the cavity [13]. The strong affinity towards organic dye molecules suggests its use for the treatment of waste water from dye industries [14].

Although CB[6] is potentially as useful as crown ethers, CDs, and calixarenes in many applications, its chemistry has not been developed much until recently because of several shortcomings. Firstly, its solubility in common solvents except for strongly acidic aqueous solution is extremely low. Secondly, no method to introduce any functional groups to the molecule was reported. Thirdly, homologues containing greater or fewer glycoluril units were not available.

Since they severely limit the scope of cucurbituril chemistry, we decided to tackle these problems when we initiated our work on CB[6] in early 1990s. After numerous unsuccessful attempts over several years, we finally succeeded in synthesis, isolation and full characterization of cucurbituril homologues containing different number of glycoluril units, and cucurbituril derivatives soluble in common solvents. These new members of the cucurbituril family have created fresh

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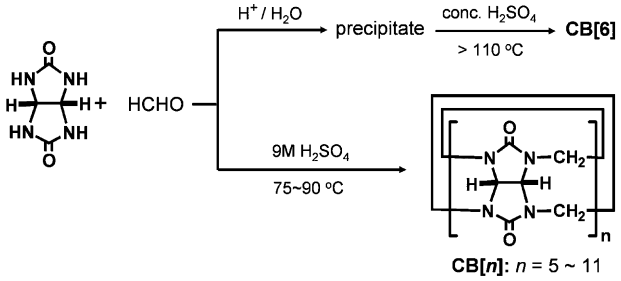
wave of interests. Within a few years a number of interesting studies have been reported. This article summarizes these recent developments, mainly based on our work in this area.

Synthesis of cucurbit[*n*]uril

The synthetic protocol of CB homologues is similar to the conventional CB[6] synthesis. Reaction of glycoluril with formaldehyde in 9 M sulfuric acid at ~75–90 °C for 24 h yields a mixture of cucurbit[*n*]uril (CB[*n*]) family. The key is the lower reaction temperature than that employed in the conventional CB[6] synthesis (>110 °C), which allows formation of significant amounts of CB homologues besides CB[6] (Scheme 1) [15]. The reaction mixture contains a family of CB[*n*] mostly from pentamer to octamer with typical contents being ~10–15% CB[5], ~50–60% CB[6], ~20–25% CB[7], and ~10–15% CB[8]. Trace amounts of higher homologues (CB[*n*], $n = 9$–11) were also detected by mass spectrometry. CB homologues are separated in pure form using fractional crystallization and dissolution [15]. Upon standing, the reaction mixture first yields crystals of CB[8]. CB[6] is then separated by fractional dissolution of other CB homologues with acetone/water. From the soluble portion, CB[5] and CB[7] are isolated and further separated by fractional crystallization.

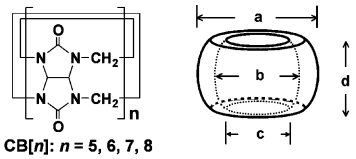


Scheme 1.

Structures and physical properties of cucurbit[*n*]uril

CB homologues CB[5], CB[7], and CB[8] have been fully characterized by various methods including X-ray crystallography (figure 1) [15]. Some structural parameters of the CB homologues are compared in Chart 1. On going from CB[5] to CB[8], the diameter of the internal cavity increases progressively from ~4.4 to ~8.8 Å. Likewise, the portal increases its diameter from ~2.4 to ~6.9 Å. In terms of cavity size, CB[6], CB[7] and CB[8] are analogous to α-, β- and γ-CD, respectively.

Solubility of CB homologues in common solvents is low ($< 10^{-5}$ M) except that CB[5] and CB[7] have a moderate solubility in water (~$2–3 \times 10^{-2}$ M), which is comparable to that of β-CD (1.6×10^{-2} M). The CB family has high thermal stability. No decomposition is observed up to 420 °C for CB[*n*] ($n = 5$, 6, and 8) although CB[7] starts decomposing at a somewhat lower temperature (370 °C).



		CB[5]	CB[6]	CB[7]	CB[8]
outer diameter (Å)	a	13.1	14.4	16.0	17.5
cavity (Å)	b	4.4	5.8	7.3	8.8
	c	2.4	3.9	5.4	6.9
height (Å)	d	9.1	9.1	9.1	9.1

Chart 1.

Host–guest chemistry of cucurbit[*n*]uril ($n = 5-8$)

CB homologues share characteristic features of CB[6], hydrophobic cavity and polar carbonyl groups

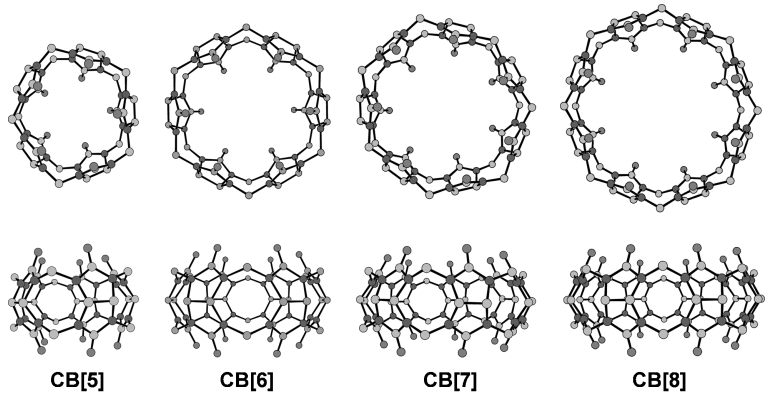
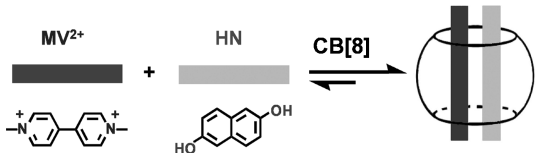


Figure 1. X-ray crystal structures of CB[*n*] ($n = 5$–8).

surrounding the portals. However, their varying cavity and portal sizes lead to remarkable molecular recognition properties different from those of CB[6] (Chart 2). CB[6] forms very stable complexes with protonated diaminoalkanes ($^{+}NH_3(CH_2)_nNH_3^{+}$, $n = 4$–7, $K > 10^5$) and moderately stable complexes with protonated aromatic amines such as *p*-methylbenzylamine ($K = \sim 3 \times 10^2$); the *o*- and *m*-isomers are not included. It can also encapsulate neutral molecules such as tetrahydrofuran and benzene in aqueous solution. On the other hand, CB[7] forms complexes with larger guest molecules that are not included in CB[6]. For example, CB[7] forms a 1:1 complex with 2,6-bis(4,5-dihydro-1*H*-imidazol-2-yl)naphthalene (BDIN). It binds protonated adamantyl amine as well as methylviologen dication (*N*,*N*′-dimethyl-4,4′-bipyridinium, MV^{2+}) in a 1:1 ratio. Neutral molecules like ferrocene and carborane get easily encapsulated in CB[7] in aqueous solution. The cavity of CB[8] is large enough to include two BDIN molecules to form a 1:2 complex, or two different guest molecules such as MV^{2+} and 2,6-dihydroxynathphalene (HN) to form a 1:1:1 complex (see below). It can encapsulate another macrocycle, such as cyclen and cyclam. The smallest homologue CB[5] can encapsulate small molecules such as N_2 in the cavity and binds strongly cations such as NH_4^+ and Pb^{++} at the portals. Two NH_4^+ ions can completely seal both the openings of CB[5].

As seen above, CBs bind guests of varying sizes similar to CDs, but the two host families have fundamental differences in host–guest interactions due mainly to the different functional groups decorating the cavity entrances. The OH groups encircling the cavity entrances of CDs can contribute to guest binding mainly through hydrogen bonding, whereas the carbonyl groups at the portals of CBs allow *charge–dipole interaction* as well as hydrogen bonding with guests, and are capable of coordination to metal ions. Such differences can be easily visualized by the electrostatic potential (ESP) profiles of CBs and CDs [12] (S.-H. Park and K. Kim, unpublished work). In CBs the regions around carbonyl oxygens are significantly negative as expected. The inner surface of the cavity is also quite negative while the outer surface is somewhat positive. On the other hand, the portal and cavity of CDs are almost neutral. Therefore, CBs preferentially bind guests with positive charge whereas CDs prefer neutral guest molecules.



Scheme 2.

The different inclusion behavior between CBs and CDs is illustrated by the electrochemical behavior of MV^{2+} in the presence of CB[7] [16, 17] and *β*-CD [18]. CB[7] binds MV^{2+} strongly ($K_{2+} = \sim 2 \times 10^5\,M^{-1}$). One-electron reduction of MV^{2+} leads to $MV^{+\bullet}$, which still binds tightly to CB[7] with a slightly lower binding affinity ($K_{+} = \sim 1 \times 10^5\,M^{-1}$) and further reduction of the guest to MV^0 substantially decreases its binding affinity to CB[7] ($K_0 = \sim 2 \times 10^2\,M^{-1}$). Therefore the complex formation constants of CB[7] towards the three species (MV^{2+}, $MV^{+\bullet}$, MV^0) follow the order $K_{2+} > K_{+} \gg K_0$, which is exactly opposite to that for *β*-CD [18].

Charge–transfer complex formation in cucurbit[8]uril

Similar to CB[7], CB[8] also forms an exclusive 1:1 host–guest complex with MV^{2+} with a formation constant of $1.1 \times 10^5\,M^{-1}$ [19]. Instantaneous and quantitative formation of an inclusion complex containing a hetero-guest pair is observed upon addition of 1 equiv of HN to the 1:1 complex of MV^{2+} and CB[8] with the formation complex of [20]. The ternary complex is also formed exclusively when their components are mixed in a 1:1:1 ratio. The major driving force for the ternary complex formation appears to be strong charge-transfer (CT) interaction between HN and MV^{2+} inside the host cavity (Scheme 2). The highly enhanced CT interaction between the two guests is probably due to their close contact within the cavity of CB[8], which has been confirmed by X-ray crystallography.

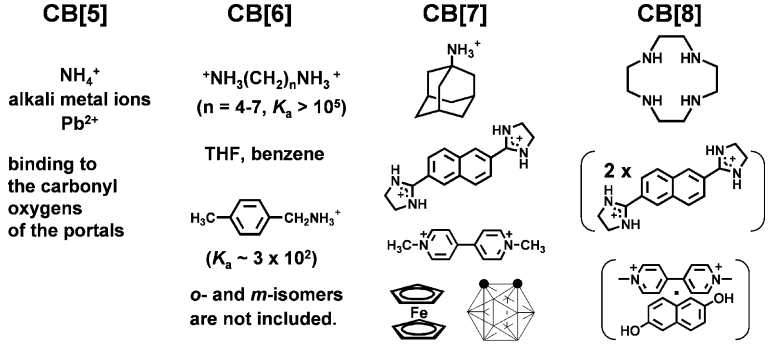


Chart 2.

Vesicle formation

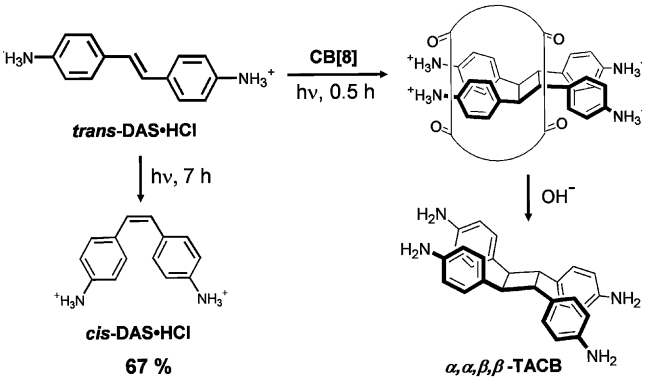
The stable CT complex formation inside a host provides new opportunities in creating elaborate supramolecular assemblies. For example, we recently studied the spontaneous formation of giant vesicles triggered by the formation of a CT complex inside CB[8] [21]. Sonication of an equimolar mixture of CB[8], viologen with a long alkyl chain, and HN in water results in a violet turbid solution. The SEM images of the complex show relatively large spheres with diameters of 0.02–1.2 μm. A high-resolution TEM image of the vesicles reveals their hollow structures. Further evidence for the formation of vesicle is provided by encapsulation of a fluorescent dye within the interior of the vesicles. Here the ternary complex behaves as a supramolecular amphiphile with a large polar head group and a hydrophobic tail. Furthermore, since the ternary complex is stabilized by CT interaction, redox chemistry can be used to trigger the collapse of the vesicles. Useful applications of this novel, supramolecular, redox-controllable vesicle system can be envisaged in many areas including drug delivery.

Macrocycle within a macrocycle

We reported a macrocycle within a macrocycle by encapsulating cyclen (or cyclam) in CB[8] [22]. The smaller macrocycles can form transition metal complexes with Cu^{II} or Zn^{II} ions while still encapsulated in the CB[8] cavity. These are the first examples of transition metal macrocyclic complexes encapsulated in molecular or supramolecular hosts. An electrochemical study revealed that the encapsulation of Cu(cyclen) in CB[8] causes a large positive shift of the $Cu^{II/I}$ redox potential and a substantial decrease in the electron transfer rates. This supramolecular system thus mimics redox-active metalloproteins in which redox centers are embedded in protein coats and may also serve as biomimetic systems for the binding, activation and catalytic transformation of specific substrates.

Cucurbit[*n*]uril-mediated chemical reactions

The cavity of CB[*n*] can be used as a reaction chamber to mediate chemical reactions. We demonstrated a facile, highly stereoselective [2 + 2] photoreaction of *trans*-diaminostilbene dihydrochloride (DAS) in the cavity of CB[8] in solution (Scheme 3) [23]. UV irradiation of an aqueous solution containing CB[8] and *trans*-DAS in a 1:2 ratio followed by a base treatment affords $\alpha,\alpha,\beta,\beta$-tetrakis(4-aminophenyl)cyclobutane almost exclusively. In the absence of CB[8], however, the main reaction pathway for *trans*-DAS upon UV irradiation is the isomerization to *cis*-DAS.



Scheme 3.

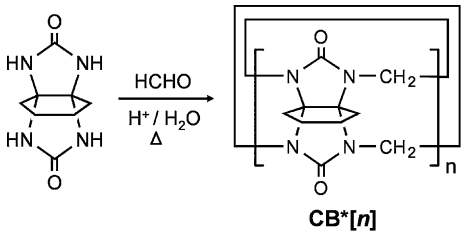
By encapsulation CB[*n*] can stabilize otherwise unstable species. For example, *cis*-DAS, which can be generated from *trans*-DAS by UV light irradiation, slowly converts to the *trans* form in the dark. However, once it forms a 1:1 host–guest complex with CB[7], the guest *does not* undergo isomerization to the *trans* form in an appreciable rate at room temperature [24].

Cucurbit[7]uril as a host for drugs

CB[7] may be used as a host for drugs of appropriate size since its aqueous solubility and internal dimensions are comparable to those of β-CD. For example, CB[7] forms a stable 1:1 complex ($K = \sim 2 \times 10^5\ M^{-1}$) with the anticancer drug oxaliplatin by encapsulating the cyclohexyl ring of the guest inside the cavity, which has been confirmed by X-ray analysis [12] (K. Kim *et al.*, unpublished work). The high stability of the complex suggests the potential use of such complexes in controlled release of drugs.

Decamethylcucurbit[5]uril ($Me_{10}CB[5]$)

The only cucurbit[*n*]uril derivative reported in the literature was decamethylcucurbit[*n*]uril ($Me_{10}CB[5]$) [25] until very recently. X-ray crystal structure of $Me_{10}CB[5]$ is nearly identical to that of CB[5] with a cavity of diameter 4 Å and portals of diameter ~2.5 Å. Bradshaw and coworkers [26] studied complexation of $Me_{10}CB[5]$ with various metal ions in formic acid/water (1:1) by calorimetric and potentiometric methods and observed that the macrocycle binds most metal ions in a 1:1 stoichiometry in the acidic solution. Interestingly, $Me_{10}CB[5]$ shows exceptionally high affinity for Pb^{2+} ion ($\log K > 9$), which may be due to the size match between Pb^{2+} and $Me_{10}CB[5]$ portals. Recently, Miyahara *et al.* [27] reported the synthesis of ammonium ion 'lid' free $Me_{10}CB[5]$, and its gas absorption and desorption properties. Gases of small (such as He, Ne, and H_2) or large diameters (such as Kr, Xe, and CH_4) compared



Scheme 4.

to the portal size are not absorbed significantly. However, gases of intermediate sizes (N_2, O_2, Ar and CO_2) are absorbed and released in cycles indicating the possible use of Me_{10}CB[5] in the solid state as a molecular sieve.

Soluble cucurbiturils (CB*[*n*])

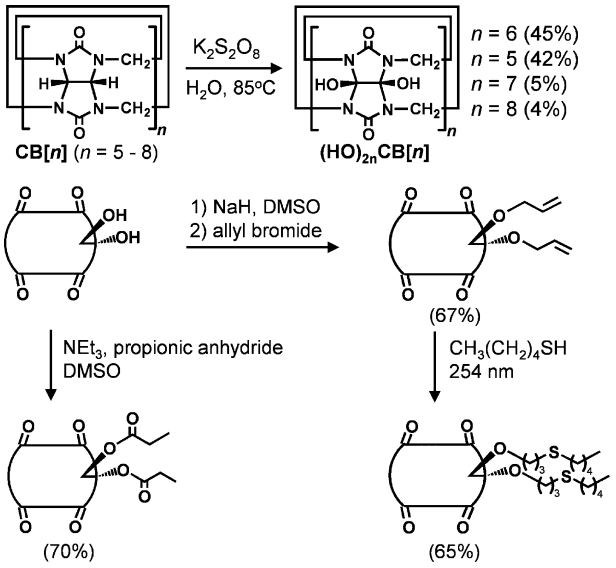
Most CB homologues and Me_{10}CB[5] are practically insoluble in common solvents limiting their use. Recently we succeeded in synthesizing new soluble CB[*n*] derivatives, CB*[*n*] ($n = 5$, 6), by the reaction of cyclohexanoglycoluril and formaldehyde (Scheme 4) [28]. The NMR data revealed cyclic pentamer and hexamer as major products in a 8:1 ratio. After a series of dissolution and fractional crystallization, CB*[5] and CB*[6] were isolated in 16% and 2% yields, respectively. Their X-ray analyses revealed the expected structures with cyclohexane rings decorating outside the "equator" reminiscent of the ringed planet Saturn. The portal and cavity sizes of CB*[5] and CB*[6] are essentially the same as those of the CB counterparts. Both CB*[5] and CB*[6] are soluble in common solvents such as water, methanol, DMF and DMSO. Interestingly, both are more soluble in water ($\sim 2 \times 10^{-1}$ M) than in organic solvents ($\sim 3 \times 10^{-2}$ M or less). The origin of their high solubility in water is not clearly understood.

The good solubility of CB*[*n*] in organic solvents allows fabrication of membrane electrodes for ion sensing. The membrane electrode prepared from CB*[6] detects acetylcholine with high selectivity over choline and other interfering ions such as Na^+, K^+, and NH_4^+. The membrane electrode made with CB*[5] behaves as an ion selective electrode for Pb^{2+}.

Recently, Nakamura and coworkers [29] reported the first unsymmetrically substituted cucurbituril, diphenylcucurbit[6]uril, (Ph_2CB[6]). The synthesis of Ph_2-CB[6] may be a route for further functionalization of the macrocycle *via* the phenyl rings.

Synthesis of cucurbit[*n*]uril derivatives *via* direct functionalization

Appending functional groups, particularly reactive ones, directly on the CB[*n*] surface is an important goal because such functionalization would pave the way to



Scheme 5.

applications of CBs in many areas, in the same manner as the upsurge in applications of CDs. This long-standing problem in cucurbituril chemistry has finally been answered through our first direct functionalization of CB[*n*] led to the formation of perhydroxyCB[*n*] ($(HO)_{2n}$CB[*n*]) [30]. This has been further modified to provide many useful CB[*n*] derivatives with desired functional groups and good solubility in common solvents. Reaction of CB[*n*] with $K_2S_2O_8$ in water produced $(HO)_{2n}$CB[*n*] as a potassium ion complex (Scheme 5). The X-ray analysis of $(HO)_{12}$CB[6] reveals the expected structure with hydroxy groups at the periphery of the CB[6] framework. Most importantly, the new CB derivative allows further functionalization and therefore several ether and ester derivatives of $(HO)_{12}$CB[6] have been generated by the conventional methods (Scheme 5). For example, perallyloxycucurbit[6]uril (AO-CB[6]) was prepared by the reaction of $(OH)_{12}$CB[6] with allyl bromide. AO-CB[6] has been used for generating many other useful derivatives through further functionalization because of its good solubility in organic solvents as well as the reactive functional group. Several applications such as anchoring CB[6] on glass surface using AO-CB[6] and its guest recognizing ability and the formation of nanosphere have been demonstrated.

Summary

This review covers new members of the cucurbituril family with specific reference to their synthesis, host–guest chemistry and application prospects. Though CB[6] was discovered nearly a century ago, the addition of new CB homologues and derivatives has widened the scope further. The past 2 years have witnessed a height-

ened interest in CB chemistry. However, the real potential of these intriguing molecular receptors is only beginning to be defined. Considering what has been done with CDs, we believe that the CB homologues and derivatives provide new opportunities in many areas of supramolecular chemistry including recognition, catalysis, sensor, transport, separation, drug/gene delivery, artificial ion channels, and nanomaterials, and many others.

Acknowledgements

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