Research Progress of Cucurbit[n]uril Analogues

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Abstract. As a new generation of host molecules, Cucurbitins have made remarkable achievements in host-guest chemistry, molecular recognition, molecular assembly, catalysis, separation detection, energy and so on. It has become a hotspot in supramolecular chemistry research. The advance of cucurbit[n]uril analogues, including glycoluril derivatives, hemicucurbit [n] uril, “handle shape” cucurbit[n]uril and heterocucurbit [n] uril is reviewed. Further researches of cucurbit [n] uril analogues are also discussed.

1. Introduction
Cucurbit[n]urils (CB[n]) is a type of macrocyclic cage compounds synthesized from the condensation of formaldehyde and glycoluril (Scheme 1), which is named because of its shape similar to that of pumpkin (Laccus: cucurbita). It was first synthesized by German chemist Behrend in 1905 [1], but it was not until 1981 that its structure was determined [2]. Subsequently, the CB[n] family rapidly expanded with the discovery of new members including CB[10] [3], CB[14] [4], CB[13] and CB[15] [5].

The structure of the CB[n] molecule has a hydrophobic, rigid cavity with hydrophilic carbonyl groups at both sides. The cavity can enclose organic small molecules, and the carbonyl groups are binding site for cations, polar compounds, and hydrogen bonds. These characteristics make it a new type of macrocyclic molecule after crown ether, cyclodextrin and calixarene. Thus it have been widely used in the fields of supramolecular catalysis, molecular self-assembly and molecular recognition [6]. However, the CB[n] also has natural defects. Firstly, it cann’t change its size according to the size of the guest molecule due to its rigidity. Second, except that the CB[5] and CB[7] are slightly soluble in water, other CB[n] are only soluble in high-concentration acid solutions, and all the CB[n] are
insoluble in organic solvents, which seriously restricts the application of CB[n] [7]. Therefore, preparation of CB[n] analogues to improve their solubility and modifiable properties has become a focus of CB[n] chemists, and has made remarkable achievements. This paper reviews the research progress of CB[n] analogues in recent years.

2. Glycoluril derivatives

The introduction of substituents at the N1 and N3, or N4 and N6 positions of glycoluril gives the nitrogen-substituted glycolurils. When this type of glycoluril derivative is condensed with formaldehyde, the bridging methylene can only be bonded on the side of unsubstituted glycoluril, and then close the ring. If the introduced substituent is active enough, it is also possible to form a new multidimensional polymer by bonding up and down.

Sindelar and co-workers [8] studied the reaction of 2,4-dimethylglycoluril (3) with paraformaldehyde in hydrochloric acid (5.4 mol/L), and obtained a novel macrocyclic compound with a yield of 30% (Scheme 2). Because of its bamboo shape and 6 units, it was named Bambus[6]uril (BU[6], if X− ions in the cavity, abbreviated as BU[6]X−).

Scheme 2. Synthesis root of BU[6].

BU[6] has a strong affinity for halogen ions and its binding ability order is I−>Br−>Cl−>F−. Thus, the product obtained by Sindelar was not the BU[6] monomer, but BU[6]·HCl. The solubility of BU[6]·HCl in water is still very low (0.02 g·L−1), but it is easy to dissolve in equimolar methanol and chloroform (greater than 90 g·L−1). Single crystals of BU[6]Cl− was obtained in solutions of methanol and chloroform solutions by adding tetrabutylammonium chloride (TABCl−). Single-crystal X-ray diffraction results showed that Cl− was in the middle of the macrocycle, while TAB+ was outside of the macrocycle, and 6 glycoluril units staggered up and down. The carbon atoms of the six methylene bridges formed a plane, and the carbonyl carbon atoms were arranged in a Z pattern above and below the plane. Obviously, the cavity of BU[6] was bigger than that of Q6 (Fig. 1).

Figure 1. Crystal structure of BU[6] without (A,B)and with(C)an included Cl−.

In order to obtain BU[6] monomer, JAN et al. [9] first replaced Cl− with stronger binding ability I− to obtain BU[6]I−, and then the I− was reoxidized to I2 with oxidizer and subsequently disengaged the cavity. The BU[6] monomer was insoluble in common solvents but can be dissolved in a mixture of acetonitrile : water (1:1) in the presence of tetrabutylammonium salt. The binding constants of BU[6] to halide ion, BF−, NO3−, and CN− were studied using 1H NMR [10]. It was found that the binding constant of BU[6] with I− in the solution of acetonitrile and water (1:1) was the largest, reaching up to
8.9×10^5 M⁻¹. The crystal structure of BU[6] and benzoic acid in chloroform with a small amount of residual water was studied [11]. Each of the two sides of BU[6] occupied one benzoic acid, and the carboxyl group interacted with a water molecule in the BU[6] cavity via hydrogen bonding (Fig. 2). Water molecule also played a similar role when p-toluenesulfonic acid was instead of benzoic acid. These results proved that the BU[6] molecular structure was more flexible, and could be adjusted according to the size of the bound ions, which had great potential applications in the field of anion recognition, elimination, and crystallization engineering.

Figure 2. Crystal structure of Complex formed by BU [6] with 2 molecule benzoates and one molecule water.

The special properties of BU[6] had also attracted the attention of theoretical chemists and related research had been carried out. The best configuration of BU[6]Cl⁻, BU[6]Br⁻, BU[6]I⁻, BU[6]OCN⁻, BU[6]SCN⁻, BU[6]SH⁻ and BU[6]CN⁻ was calculated using quantum mechanics density functional theory [12]. The results showed that the anions were located inside the cavity and that these anions formed 12 weak hydrogen bonds with the methylene hydrogen atoms in the glycoluril unit, while the corresponding cation had a weak interaction with the carbonyl group. In addition, Gejji et al. [13] studied the electronic structure, vibrational spectroscopy, and ¹H NMR of BU[6] combined with halide ions.

When synthesizing different kinds of substituted BU[6], the size of the ring can be controlled by the template. In the presence of a catalytic amount of p-toluenesulfonic acid (PTSA), 2,4-dibenzylglycoluril (4) reacted with paraformaldehyde to form an octabenzyl-substituted Bambus[4]uril (Bn8BU[4]). When the anion was used as a template, the main product was changed to dobezenyl substituted Bambus[12]uril (Bn12BU[6]) (Scheme 3). After screening various anions, it was found that when using tetrabutylammonium iodide (TBAI), the yield of Bn12BU[6] was the highest, reaching to 65% [14].

Scheme 3. Reaction between 2, 4-dibenzylglycoluril and formaldehyde under different conditions.

Using different catalytic conditions, a variety of BU[n] analogs (Fig. 3) can be synthesized from allyl-glycoluril (Scheme 4) [15]. Under microwave conditions (200 W), 5 reacted with formaldehyde in a solution of 0.07 mol/L PTSA in CHCl₃ at 75 °C for 2 h to generate product 8 (yield 85%). However, 5 with formaldehyde in a toluene solution of 0.01 mol/L PTSA at 110 °C for 4 h were found to give 9 in the presence of TBAI (yield 60%). Surprisingly, 8 would give 10 by isomerization when Hoveyda-Grubbs II catalyst was used. Also, the above catalyst can catalyze the reaction of 8 with 1-hexene to
give product 11 (yield 20%). In ethanol solution, product 12 could be synthesized by 10% Pd/C catalytic hydrogenation of 8.

![Scheme 4. Preparation of diallyl glycoluril 5.](image)

**Figure 3.** Synthesized new bambusurils.

The improvement of the dissolution performance is also an important direction for the research of novel BU[\(n\)] compounds. 13 was found to have high solubility in pure water, a consequence of the benzoic acid functional group (Scheme 5) [16]. Its binding constant with anion in pure water reached up to 10^7 L·mol⁻¹, which can be used as a novel anion neutral receptor. In addition, it had a strong selectivity for ClO₄⁻ and F⁻ ions as a results of their great difference of binding constants (5.0×10^5 fold).

![Scheme 5. Synthesis of the water-soluble bambusuril macrocycle.](image)

Wang et al. [17] synthesized a novel CB[\(n\)] analogue: Me₅TD[5] (Scheme 6). Its structure was similar to CB[\(n\)], but with a smaller port diameter and cavity volume. It is worth noting that it could dissolve in water and common organic solvents. The study also found that it could self-assemble with para-xylidenediamine hydrochloride to form a linear supramolecular polymer (Fig. 4).
In addition, thio-CB[n] can be synthesized using thio-glycouril. The density functional theory calculation results showed that the molecular structure and electronic arrangement of the thio-CB[n] was similar to that of the thio-CB[n], but the former had a lower HOMO–LUMO energy gaps than the latter, and thus had good coordination with transition metal ions [18]. Quantum chemical calculations of assembled nanochannel structures of thio-CB[n] and transition metals such as Pd²⁺, Pt²⁺ and Hg²⁺ showed that the growth of nanotubes can only start from one side of the assembly, and thus can be used as a molecular wire, which had important application value in Nano electronics [19].

3. Hemicucurbit[n]uril
The structure of the hemicucurbit [n] uril is only half that of the CB[n], and it can be dissolved in organic solvents such as alcohol and chloroform, which makes it possible to study the properties and application of the CB[n] compounds in organic solvents.

Equal amounts of imidazolidin-2-one (14) and formaldehyde were reacted in 4 mol/L HCl at room temperature for 30 minutes to give a cyclic hexamer, so-called hemicucurbit[6]uril (hemCB[6]) (Scheme 7) [20]. The cavity of the former product contained HCl molecules that can be removed by drying in a vacuum at 80 °C.

When above reaction was carried out at 55°C, a twelve-membered ring hemicucurbit [12] combining two water molecules was obtained (Scheme 8). However, water molecules were extremely difficult to remove, even at 80°C for 18 hours in vacuum.
Scheme 8. Synthesis of hemCB [12].

The reaction of cyclohexyl-imidazolidone with paraformaldehyde in 4 mol/L HCl at 70 °C led to the formation of cyclohexyl-hemicucurbit[6]uril (hmcyCB[6]) (Fig. 5) [21]. Different types of single crystal structures can be obtained using different solvent systems, hmcyCB [6] can enclose solvent molecules in the center, and their high selectivity to CHCl₃, CHCl₂ and CCl₄ may be related to the symmetry of solvent molecules.

Figure 5. Chemical structure of hmcyCB[6].

4. Handle shape cucurbit[n]uril
Under mild conditions, Isaacs et al. [22] synthesized a variety of glycoluril linear polymers including dimerization, trimerization, tetramerization, pentamerization and hexamerization. By condensing two glycoluril trimers with different dialdehydes under acidic conditions, inverted-CB[n] or bis-nor-seco-cucurbit[n]uril can be obtained, which enables us to further understand the synthesis mechanism of CB[n]. Based on the above results, Derick et al. [23] reported the synthesis of 17, 21, 22, 23 and 25 by the reaction of glycoluril hexamer (15) with the compounds 16, 18, 19, 20 and 24 in 9 mol/L H₂SO₄ or concentrated HCl (Sheme 9), respectively.
Isaacs's group \[24\] prepared a new handle shape cucurbit[n]uril \(27\) by using 23 as starting material, condensed with propargyl bromide, followed by cyclization with azide compound (yield 75\%) (Scheme 10). There was a group of an isobutylammonium in 27, and 2 molecules of 27 self-assemble to form a daisy chain assembly. Surprisingly, this assembly was exceptionally stable to temperature and interference with different metal ions. Even the assembly of 27 with spermine in water was particularly susceptible to disassembly, forming a two-molecule 27 self-assembly.

Vladimir Sindelar et al. \[25\] first reported the reaction of glycoluril, paraformaldehyde, and substituted aldehydes in concentrated HCl to give a bridged methylene-substituted CB\([n]\) (Scheme 11).
Its interaction with a series of alkyl salts showed that there were no significant changes of properties compared to CB.

![Scheme 11. Synthesis of monosubstituted CB [6].](image)

After successful oxidation of CB[n] with persulfate to give hydroxy-CB[n], Scherman [26] successfully isolated (HO)nCB[6] using a reversed-phase macroporous resin. The resulting compound can be further derivatized to obtain other handle shape CB[n], which provided a new and efficient way to prepare handle shape CB[n].

5. Heterocurbit[n]uril
Isaacs and co-workers [27] reported the synthetic method of a novel CB[n] analogue: boat shape CB[n]. In the presence of PTSA, ethyl formate-glycolurea (28) was refluxed in 1,2-dichloroethane to prepare glycoluril oligomers (29-31) (Scheme 12), followed by cyclization of the resulting glycoluril oligomers with 35 (Scheme 13). Through the study of the fluorescence effect of the host or guest molecule, it was found that the boat shape CB[n] had a better binding ability than that of the CB[6], and it also showed the aromaticity that CB[n] and cyclodextrins didn’t possess.

![Scheme 12. Controlled oligomerization of 28](image)

*Conditions: (a) CICH₂CH₂Cl, PTSA, reflux; (b) CH₃CH₂NH₂, 75°C, 68%; (c) CICH₂CH₂Cl, PTSA, reflux, 38%; (d) LiOH, H₂O, CH₂OH, 89%
Subsequently, Isaacs and co-workers [28] discovered that these oat shape compounds were kinetically controlled products and proposed a reaction mechanism. Molecular recognition properties of a water-soluble CB[n] analogue with a series of small guest molecules such as alkyl diamines, aromatics, amino acids, in a buffer solution (sodium acetate, 50 mM, pH 4.74, 25 °C) using fluorescence spectroscopy [29]. It was found that the binding constants of water-soluble CB[n] analogue and alkylamines (H₂N(CH)ₙNH₂, n=6,7,8,9,10,11,12) raised with the increasing of alkyl chain. Due to the π-π stacking, the constant (Ka) with aromatic is reaching up to 10²–10⁶ M⁻¹. The binding constant to amino acids and nucleobases were approximately 10³–10⁶ M⁻¹.

The macrocyclic compound 41 derived from 5-tert-butyl-1,3,5-triazacyclohexanone was readily to form a self-assembled structure (Scheme 14) [30]. The self-assembled single-crystal structure showed that the two urea groups were located above and below the macrocyclic plane, respectively, the two benzene rings were parallel and slightly inclined to the macrocyclic plane, and there was no hydrogen bonding in the molecule. The molecules of compound 41 were superposed on each other to give a stable tubular assembly (Fig. 6). The urea groups above and below the molecule were connected by hydrogen bonds, and the slightly inclined benzene ring counteracted the π-π stacking action between the aromatic rings, making the assembly more stable.

Scheme 13. Cucurbit[n]uril analogues.

Figure 6. Schematic representation of the self-assembly of rigid macrocyclic bis-ureas.
Scheme 14. Synthesis of bis-urea macrocycle 41. Reagents conditions: (a) meta- dibromoxylene, NaH, THF, 20%, (b)20% diethanolamine, MeOH, reflux, 66%.

The single crystal structure of macrocyclic compound 42 synthesized from 2, 7-dibromomethylnaphthalene (Scheme 15) showed that it had a bowl-like structure, and the two urea groups were in parallel with each other (Fig. 7). In addition, 42 had two different solvated single crystal structures, 42·DMSO·(H₂O)₂ and 42·(MeOH)₂, which had a large difference in conformation [31].

Scheme 15. Synthesis of 42. Reagents and conditions: (a) NaH, 5-tert-butyl tetrahydro- 1, 3, 5-triazin-2(1H)-one, THF (b) 20% diethanolammonium chloride aqueous solution in methanol.

Figure 7. Crystal structure of naphthalene macrocycle 42. (A) Macrocycle shows a bowl shape orientation of the Naphthalene spacers. (B) Angle between the naphthalene and urea is strained to 115° from ideal 120°. (C) Side view of macrocycle shows a 6° tilt of the ureas from perpendicular to the plane of the macrocycle.

Compound 43 can be synthesized by a similar synthesis method (Scheme 16), which can be self-assembled to form a large cavity and stable columnar channel. The results of porosity and adsorption studies showed that this columnar channel can efficiently and selectively catalyze the coumarin to formation trans-head to head dimers (Fig. 8) [32]. Further studies had shown that compound 43 can catalyze the photodimerization of coumarin, 6-methyl coumarin, 7-methyl coumarin and terpenes under UV irradiation [33].
Scheme 16. Synthesis of 43. Reagents and conditions: (a) Pd(PPh$_3$)$_2$Cl$_2$/CuI/piperidine, 0 °C, 3 h, 97%; (b) NBS/PPh$_3$ in THF, 0 °C, 12 h, 87%; (c) triazinane, NaH/THF, reflux 48h, 22%; (d) 1:1 MeOH:(20% NH(CH$_2$CH$_2$OH)$_2$ in H$_2$O, PH~2), reflux 12 h, 96%.

Scheme 17. Synthesis of 44. Reagents and conditions: (a) tert-butyl triazone, NaH, THF, 20%. (b) 20% diethanol amine, MeOH, reflux, 85%.

If the starting material changed to ketone, compound 45 can be obtained using a similar route (Scheme 18). Although 45 and 44 were similar in size and binding constant to the same guest molecule, these two host molecules had different catalytic effects on guest molecules. The [2+2] polymerization reaction was catalyzed by 44 with higher yield and selectivity, while compound 45 can promote photo isomerization reaction (Fig. 9) [35].

Figure 8. The selective photodimerization of coumarin.

Compound 44 can self-assemble into nanotubes through hydrogen bonding between urea groups and π-π stacking between aromatic rings [34]. The nanotubes can bind acetic acid molecules reversibly, and be stable at 180 °C, which can be used as a reusable molecular sieve.
The benzophenone group in compound 45 was originally a photosensitizer, and thus singlet oxygen can be generated by irradiation with ultraviolet light in an oxygen-containing solvent [36]. The stable solid host-guest complex can be formed using 45 with 2-methyl-2-buten e and isopropyl benzene, and the selective oxidation reaction occurred when these complexes were irradiated with ultraviolet light. 2-methyl-2-buten e was selective oxidation to 3-methyl-2-butene-1-ol (90% selectivity), and cumene was selective oxidation to α,α'-dimethyl benzyl alcohol (63% selectivity), during which no peroxides, hydroperoxides and other by-products were produced. The above results are of great significance for the development of green oxidants.

Ehud Keinan et al. [37] reported the synthesis of a series of macrocyclic compounds that were heterozygous for aromatic compounds and ureas (including thioureas) (Scheme 19 and Scheme 20). These reactions had the advantages of multiple synthetic pathways, mild reaction conditions, and inexpensive raw materials, and were therefore easily realized. Among them, thiourea compounds had a
stronger ability to react with metal ions, and post-reaction treatment was easier. The controllable ring size can be achieved using different unit reactions, and the macrocyclic compound itself can adopt multiple conformations to flexibly bind with the guest molecules, which allowed the preparation of a specific macrocyclic host molecule according to the needs of the guest molecule.

Scheme 19. Synthesis of multifarenes 51, 52 and 53. (a) 54(1 eq.), 55(4 eq.), (CH$_2$O)$_n$(3 eq.), PTSA H$_2$O(30 mol%), toluene, 65 °C, 2 d; (a') same as (a) but with 1.5 eq. of 54 and 1.0 eq of 55; (b) 54(1 eq.), 55(1 eq.), (CH$_2$O)$_n$(10 eq.), PTSA H$_2$O(30 mol%), toluene, 55 °C, 6 d; (c) 56(1 eq.), 55(1 eq.), (CH$_2$O)$_n$(4 eq.), PTSA H$_2$O(50 mol%), toluene, 60 °C, 2 d; (d) 57(1 eq.), 55(1 eq.), (CH$_2$O)$_n$(5 eq.), PTSA H$_2$O(2 eq.), toluene, 60 °C, 2 d; (e) 1,2-diaminoethane(DAE, 1 eq.), NaClO$_4$(4 eq.), AcOH-MeOH, reflux, 24 h; (f) DAE(1 eq.), CH$_3$CN-MeOH, -10 °C, 8 h; (g) Mg(OAc)$_2$·4H$_2$O(0.5 eq.), DAE(1 eq.), Mg(NO$_3$)$_2$·6H$_2$O(0.5 eq.), reflux, 8 h; (h) NaBH$_4$, MeOH, 0 °C to rt, 2 h; (i) TDCI, dry THF, rt, 3 h.
Scheme 20. Synthesis of multifarenes 66, 68 and 69. (a) 58(1 eq.), 2-imidazolidinone (1 eq.), (CH$_2$O)$_n$ (5 eq.), PTSA.H$_2$O (50 mol%), toluene, 60 °C, 2 d. (b) 57(1 eq.), 67(1 eq.), (CH$_2$O)$_n$ (2.1 eq.), PTSA.H$_2$O (50 mol%), toluene, 70 °C, 3 d. (c)63(1 eq.), CDI (3.3 eq.), dry THF, RT, 2.5 h.

6. Conclusion
So far, great progress has been made in the synthesis of CB[n] analogues, but there is still a lot of work to be done. For example, development of new glycoluril substitutes, preparation of CB[n] analogues with different degree of polymerization and different substituents, and formation of heterocuburit[n]uril by methylene bridges, as well as the properties and applications of these new CB[n] analogues and their host-guests, etc. It is believed that as people's efforts and research deepen, more and more excellent melon analogues will constantly spring up.

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