

Review

Development of hydroxylated cucurbit[*n*]urils, their derivatives and potential applicationsRui Han Gao^a, Li Xia Chen^a, Kai Chen^{b,*}, Zhu Tao^a, Xin Xiao^{a,*}^aKey Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, PR China^bJiangsu Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, PR China

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ABSTRACT

Cucurbit[*n*]urils (Q[*n*]s), a relatively new class of macrocyclic hosts with a rigid hydrophobic cavity and two identical carbonyl-fringed portals, have attracted much attention in supramolecular chemistry. Compared to the chemistry of cyclodextrins and calixarenes, the development of cucurbit[*n*]uril chemistry has been relatively slow, mainly due to the high chemical stability of Q[*n*]s, which makes them difficult to functionalize. The discovery of the direct oxidation method to yield perhydroxylated cucurbit[*n*]urils {(HO)_{2n}Q[*n*]s} greatly promoted Q[*n*] chemistry, since (HO)_{2n}Q[*n*]s can serve as a platform trigger for the synthesis of many other functionalized cucurbit[*n*]urils. The resulting products have attracted much attention for numerous potential applications. In this review, we summarize developments based on derivatives of cucurbit[*n*]urils hydroxylated at the “equatorial” positions, as well as the potential applications of these molecules.

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* Corresponding authors.

E-mail addresses: gaoruihan.1989@163.com (R.H. Gao), chenlixia19@163.com (L.X. Chen), kaichen85@nuist.edu.cn (K. Chen), gzutao@263.net (Z. Tao), gyhxxiaoxin@163.com (X. Xiao).<http://dx.doi.org/10.1016/j.ccr.2017.07.017>

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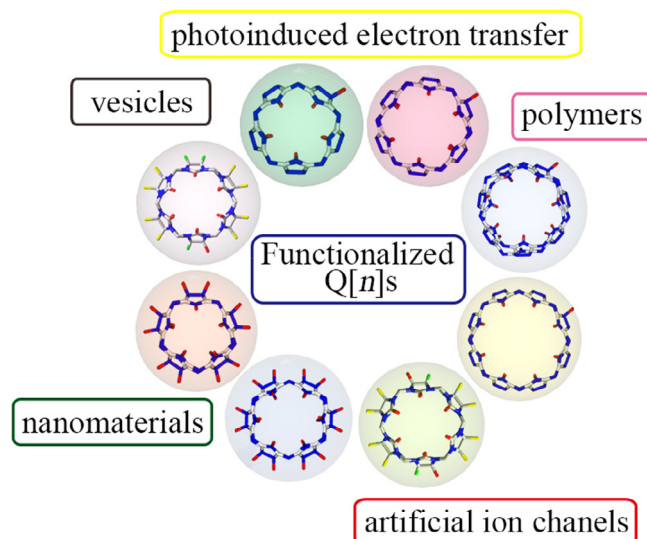
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1. Introduction

Cucurbit[n]urils (commonly abbreviated as Q[n]s or CB[n]s) are among the macrocyclic receptors known to date, and rank alongside crown ethers, cryptands, cyclodextrins, and calixarenes. Cucurbit[6]uril (Q[6]) was first synthesized by Behrend and co-workers in 1905 [1], yet its chemical nature and structure remained unknown until 1981, when a full characterization was reported by Mock and co-workers [2]. Soon after, the supramolecular chemistry of Q[6] was further developed in the 1980s and 1990s as a result of the pioneering work of Mock, Buschmann, Kim and their co-workers [3–5]. In 2000, the research groups of Kim and Day successfully isolated and achieved X-ray characterizations of Q[5], Q[7], and Q[8] [6–8]. Less than two years later, Day and co-workers crystallized Q[10] and identified its structure [9]. The pumpkin-shaped Q[n]s, with a hydrophobic cavity and two identical carbonyl-fringed portals, led to tremendous growth in the fields of Q[n]-based host–guest chemistry [10–29] and coordination chemistry [30–35]. While great progress has been achieved in this chemistry, two main limitations still preclude cucurbit[n]urils from many potential applications. First, cucurbit[n]urils have poor solubility in most common organic solvents, and, in particular, the Q[n]s with even numbers such as Q[6], Q[8], and Q[10], even have very low solubility in water (<0.1 mM). Second, it is a challenging task to introduce functional groups on the skeletons of Q[n]s. To overcome the low solubility in water and common organic solvents, alkyl-substituted glycolurils have been used in place of glycoluril as the synthetic precursor, and a series of fully and partially alkyl-substituted Q[n]s has been synthesized and exploited [36]. Dimethylglycoluril was the first alkyl-substituted glycoluril employed to synthesize fully methyl-substituted Q[n]s, as described by Stoddart and co-workers in 1992. Unexpectedly, only dexamethylcucurbit[5]uril (Me₁₀Q[5]) was obtained, and its solubility in water and common organic solvents was not significantly improved [37]. However, Kim and co-workers succeeded in the synthesis of two fully cyclohexano-substituted cucurbit[n]urils ($n = 5, 6$; CyH_nQ[n]s) by the condensation of cyclohexanoglycoluril with formaldehyde in an acidic medium. These molecules proved to be soluble not only in neutral water, but also in some organic solvents, such as methanol and ethanol [38]. Our group synthesized a series of hemimethyl-substituted cucurbit[n]urils (HemiMeQ[n]s) by using 3 α -Methylglycoluril as a precursor, including two HemiMeQ[5] isomers, two HemiMeQ[6] isomers, and a HemiMeQ[7] isomer [39–41]. The hemimethyl-substituted cucurbit[n]urils are readily soluble in both water and dimethyl sulfoxide (DMSO). Indeed, the HemiMeQ[7] isomer is the most water-soluble member of the whole Q[n]-family identified to date [41]. More recent research has revealed that the twisted cucurbit[n]urils ($n = 13, 14, 15$), the largest Q[n]s yet characterized, can also dissolve in both neutral water and DMSO [42,43]. Thus, fully or partially alkyl-substituted Q[n]s and even the tQ[n]s can solve the issue of low solubility of Q[n]s.

Kim and co-workers first solved the second limitation, that is, the functionalization of Q[n]s, in 2003. They prepared a series of hydroxy-substituted (HO)_{2n}Q[n]s by simple oxidation of the corresponding Q[n]s with K₂S₂O₈ in water [44]. The resulting (HO)_{2n}Q[n]s have since served as starting materials for the synthesis of many

other functionalized cucurbit[n]urils, which have been applied in artificial ion channels, vesicles, photoinduced electron transfer, polymers, nanomaterials, and so on (Scheme 1) [45–51]. In addition, Day and co-workers recently demonstrated a new carboxylated pentacyclohexanocucurbit[5]uril (AcidCyp5Q[5]), bearing a COOH group at the apex of each of its five glycoluril moieties, but no further derivatives have apparently been reported [52]. Unfortunately, the synthesis of (HO)_{2n}Q[n]s has been hampered by decomposition of large amounts of the starting Q[n]s; in particular, for larger Q[n]s, such as Q[7] and Q[8], the yields were too low for practical use, and for alkyl substituted cucurbit[n]urils (SQ[n]s), hydroxylation was even less successful. Although a straightforward procedure for introducing one or more points of chemical attachment on the outer surface of perhydroxylated cucurbit[n]urils ((HO)_{2n}Q[n]s) is possible in principle, this would not guarantee a high level of control over molecular structures unless limited substitution patterns, such as mono- or dihydroxylated cucurbit[n]urils ((HO)Q[n]s and (HO)₂Q[n]s), were used in such a procedure. Two main routes have been used for the synthesis of mono-functionalized Q[n]s: Isaacs and co-workers established a method by reacting C-type glycoluril oligomers, such as the C-glycoluril hexamer precursor, with a suitably functionalized glycoluril to afford a monofunctional Q[n] [46–55]; Scherman and co-workers first prepared monohydroxycucurbit[6]uril using persulfate salts [45] in a method modified from that described by Kim [44], but this method is not generally applicable to larger Q[n]s such as Q[8], or to SQ[n]s. In 2013, Bardelang and Ouari developed a controlled photochemical method using hydrogen peroxide and UV light [56,57], whereby a limited number of alcohol functional groups can be directly introduced on any selected cucurbit[n]uril, including Q[5]–Q[8] and alkyl-substituted Q[n]s. This method has been successfully utilized in our laboratory for oxidation [58]. These methods for preparing functionalized cucurbit[n]urils could open up new research topics in Q[n] chemistry, supramolecular architectures, and functional materials.



Scheme 1. Hydroxylated cucurbit[n]urils and its application.

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