Emerging Macrocyclic Arenes Related to Calixarenes and Pillararenes

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7.1   Introduction

Design and synthesis of macrocyclic compounds are always one of the cutting-edge research topics since the birth of supramolecular chemistry [1–5]. From Pedersen's groundbreaking discovery of crown ethers in the mid-1960s [6, 7], countless macrocyclic hosts have been impelling the development of host-guest and supramolecular chemistry [8–12]. Among them, macrocyclic arenes comprising of multi-aromatic units have made a great contribution owing to their easy accessibility and selective host-guest properties. The most representative case is definitely the calix[n] arene family (calixarenes for short) [13, 14], being considered as the third generation of star supramolecular host. Their structure and conformation properties, post-modification methods, host-guest properties, and supramolecular functions have been intensively studied [15–19]. Besides that, pillar[n]arenes (pillararenes, or pillarenes for short) [20], a relatively new family of synthetic macrocyclic arenes, have also gained wide attention due to their unique and outstanding binding properties and ease of application development during the last decade [21–29], which have also been regarded as the fifth generation of star supramolecular host after cucurbit[n]urils [30].

However, in spite of many significant advances in calixarene and pillarene families, the design and exploration of new synthetic macrocyclic receptors are still an everlasting and challenging topic in supramolecular macrocyclic chemistry. In the last few years, scientists have reported several new families of synthetic macrocyclic arenes, inspired by the rapid development of calixarene and pillarene chemistry. Therefore, we take this good opportunity to give a brief overview of these newly designed macrocyclic receptors, especially with the focus on their syntheses, structures, chemical functionalization, and host-guest properties. We believe that it will be a timely and valuable reference for those who have been engaged in or are interested in the design and development of macrocyclic compounds.

7.2   New Macrocyclic Arenes Related to Calixarenes

7.2.1   Calix[2]arene[2]triazines

Calix[2]arene[2]triazines (**1**–**8**) as a new class of heteroatomic calixarene derivatives were first reported by Wang and coworkers in 2004 [31]. These macrocycles can be easily obtained through a high yielding fragment coupling approach with cyanuric chloride and resorcinol as the ring-forming monomers (Fig. 1a, b). The single crystal structures of calix[2]arene[2]triazines (**1**–**8**) show a 1,3-alternate conformation with two benzene rings almost perpendicular to the plane of the four bridging hetero-atoms. And, the bridging heteroatoms are more inclined to form a conjugation system with the triazine rings rather than the benzene rings as a result of the intramolecular/intermolecular steric and electronic effects. In addition, the cavity features of calix[2]arene[2]triazines, i.e., the distances and inclined angles between
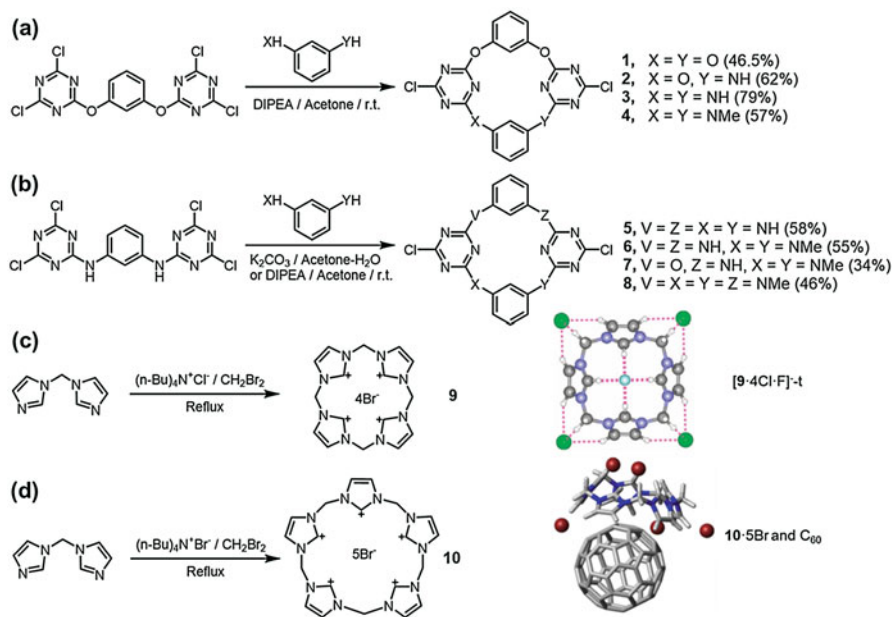
Fig. 1 (**a, b**) Synthetic routes and chemical structures of calix[2]arene[2]triazines (**1–8**) [31]; (**c**) synthetic route to calix[4]imidazolium (**9**) and the B3LYP self-consistent reaction field (SCRF) polarizable continuum model (PCM) optimized geometry of the cone conformer of [**9**·4Cl·F]⁻-t [32]; (**d**) synthetic route to calix[5]imidazolium (**10**) and the most stable geometry of the complex composed of neutral C_{60} fullerene and **10**·5Br [32]

two benzene rings, were strongly influenced by the species of the bridging hetero-atoms, which endows the calix[2]arene[2]triazines with great potentials in cavity and electron-controllable molecular recognition process.

7.2.2 Calix[n]imidazoliums

Homo-calix compound, calix[4,5]imidazolium (**9**, **10**), with four or five positively charged imidazolium moieties was first reported by Kim and coworkers in 2013 [32]. **9** and **10** could be easily synthesized through a template-directed synthesis with Cl⁻ and Br⁻ as the template anions during the ring closure process (Fig. 1c, d). The single crystal structure analyses demonstrated a cone-shaped conformation stabi-lized by multi-noncovalent (C-H)⁺/π⁺-anion interactions between the halogen ions and the imidazolium rings. More importantly, **9** exhibits a strong binding affinity toward fluoride ($8 \times 10^{4}\,\mathrm{M^{-1}}$), which ensures its great potential in fluoride detection and removal. Meanwhile, **10** with more imidazolium moieties and larger size of cavity showed a specially selective recognition toward fullerenes via the well-known noncovalent π⁺-π interactions (Fig. 1d), which can even make C_{60} soluble in water.

7.2.3 Tetraphenylethylene (TPE)-Based Oxacalixarenes

Oxacalixarenes, a class of homocalixarene derivatives with tidy synthetic ease and outstanding host-guest properties, have received much attention [33, 34]. In 2014, taking advantages of both oxacalixarene and TPE, Zhang, Zheng, and coworkers synthesized a novel TPE-based expanded oxacalixarene (11) through the well-known S_NAr reaction by condensation of dihydroxytetraphenylethylene with 2,6-dichloropyrazine in DMSO in the presence of Cs_2CO_3 catalyst [35]. Interestingly, the conformation of 11 in the crystalloid state could be easily altered by the trapped guests, and two kinds of supramolecular grid networks could be clearly realized (Fig. 2a). Afterward, the TPE-based oxacalixarene was first be used to construct a porous tricyclooxacalixarene cage (12) (Fig. 2b), which could further establish a grid-like porous structure in accompany with a remarkable adsorption capacity for carbon dioxide [36]. Very recently, by inducing the TPE-based oxacalixarene cage (TOC) to framework, Zhang, Zheng, Tan, Liu, and coworkers successfully constructed a cage-based emissive polymeric framework (pTOC) (13) [37]. Compared to monomer TOC, the pTOC conquers the problem of window-to-arene packing modes of cages and enlarges their pores (Fig. 2b). Particularly, the pTOC

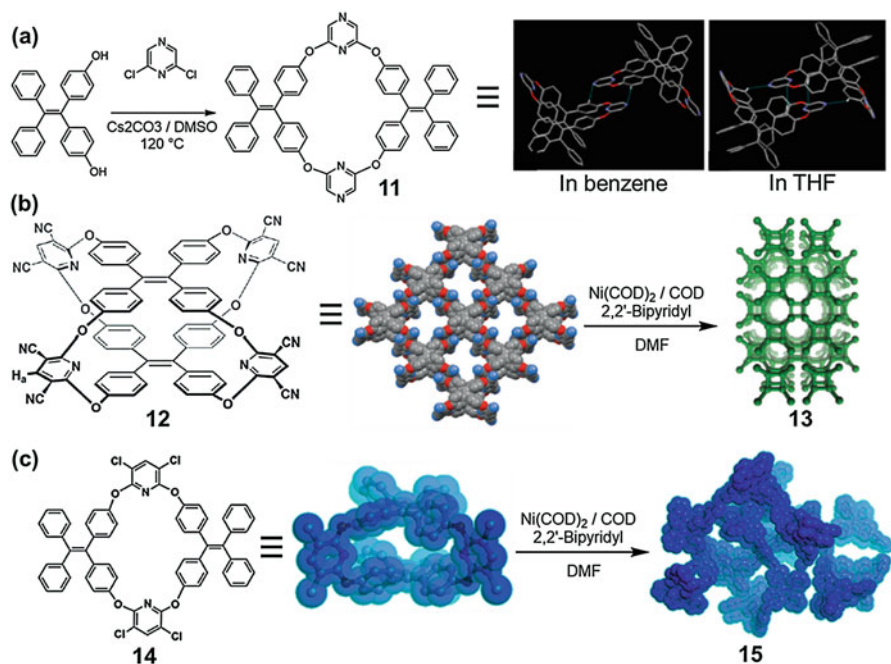**Fig. 2** (**a**) The synthetic route to the TPE-based expanded oxacalixarene (11) and its single crystal structures obtained from its solution of benzene (left) or THF (right) [35]; (**b**) the synthetic route to the cage-based emissive polymeric framework (pTOC) (13) from the tricyclooxacalixarene cage (12) [36, 37]; (**c**) the synthetic route to the porous organic polymer (15) from the TPE oxacalixarene macrocycle (14) [38]

rendered a reversible fluorescence enhancement in the presence of CO_2 and a recovery with CO_2 released. Following this stimuli-responsive property, pTOC could be used for detecting and quantifying trace amount of CO_2 among multiple gas mixtures. Similarly, a TPE oxacalixarene macrocycle (**14**) with high fluorescence quantum yield (70%) was synthesized by a similar method in 2018 [38]. As depicted in Fig. 2c, **14** as the monomer could be utilized to construct a porous organic polymer (**15**), which presented a decent Brunauer–Emmett–Teller (BET) surface area, specific pore volume, and fluorescence emissive properties. According to the Förster resonance energy transfer (FRET) effect, **15** with blue-greenish emission could be changed to a white-light emission material upon complexation with tris(bipyridine)ruthenium (Ru^{2+}) as its complementary emission color.

7.2.4 Hybrid [n]Arenes

Through a hybrid approach, hybrid [n]arenes were constructed efficiently by Szumna and coworkers in 2015 [39]. This medium-sized macrocyclic compound with different alkoxybenzene units could be directly produced by condensation of two commercially available alkoxybenzene monomers and formaldehyde as catalyzed by trifluoroacetic acid (TFA) (Fig. 3a). Generally speaking, hybrid [4]arenes consisting of four alkoxybenzene units (**16–19**) are usually in a [2 + 2] or [3 + 1] composite pattern. However, with the condensation of **18** and **19**, a novel hybrid macrocycle with [3 + 2] composite pattern could be facilely captured and isolated. For the confirmation of the reversibility of the hybrid-forming reaction, a "scrambling" experiment by reaction of two conventional macrocyclic arenes based on mono-benzene units was adopted. Subsequently, the results demonstrated that the reaction was absolutely reversible and the distribution of the products was thermodynamically controlled. In a word, this acid-catalyzed thermodynamically favored hybrid approach is very efficient and convenient.

Following this work, Yu and coworkers designed the first [2 + 1] pattern biphenyl-type hybrid [3]arene (**20**) in 2016 (Fig. 3b), which is composed of two 1,3,5-trimethoxybenzene units and a 4,4-biphenol diethyl ether unit linked with methylene bridges and exhibited a good binding affinity toward 1-dihexylammonium hexafluorophosphate [40]. Then, Szumna and coworkers synthesized a type of anthracene-based hybrid [4]arene (**21**) by using 1,4,5,8-tetramethoxyanthracene and 1,3-dimethoxybenzene as the cyclic-forming monomers in 2017 (Fig. 3c), which could be further used to recognize pyridinium iodide in chloroform due to its extended cavity [41].

7.2.5 Calix[3]carbazole

In 2016, via a convenient one-step approach, a bowl-shaped calixarene derivative named calix[3]carbazole (**22**) was efficiently obtained by Yang and coworkers (Fig. 3d) [42]. Compared to many conventional carbazolyl-based macrocycles [43,
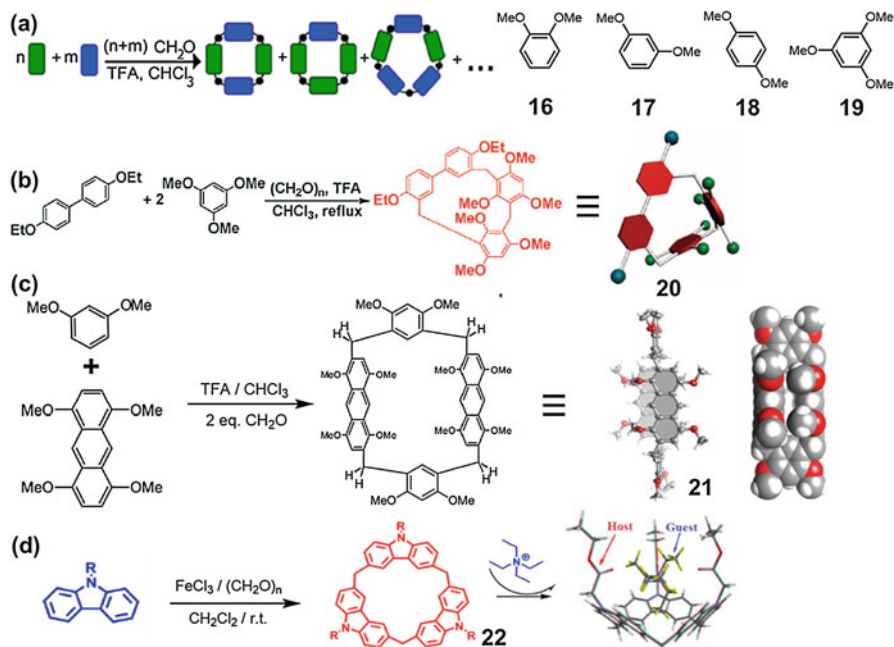
Fig. 3 (**a**) Synthetic route to hybrid [n]arenes and the monomers used in the construction of hybrid [n]arenes [39]; (**b**) synthetic route to the biphenyl-type hybrid [3]arene (**20**) [40]; (**c**) synthetic route to the anthracene-based hybrid [4]arene (**21**) and the single crystal structure of **21** [41]; (**d**) the synthetic route to **22** and an energy-minimized model of the complex of calix[3]carbazole (**22**) with $N(C_2H_5)_4^+$ cation guest [42]

44], **22** was obtained in a simpler synthetic method with a higher yield (20%). Not only the desirable product (**22**) could be facilely obtained, some by-products, i.e., calix[4–6]carbazole, could also be captured and verified simultaneously. Moreover, molecular recognition experiments and energy-minimized models demonstrated that **22** possesses a preferential binding affinity and optical response to tetra-ethylammonium cation guest via cation−π interactions. Owing to its large π-cavity and chromophoric property, this new class of macrocyclic arenes possesses great potentials in the fields of ion sensing and molecular recognition.

7.2.6　Cyclo[4]carbazole

A new macrocyclic receptor, cyclo[4]carbazole (**23**), was successfully synthesized by Huang and coworkers in 2016 [45]. Cyclo[4]carbazole **23** could be facilely obtained through a fragment coupling method by the reaction of the carbazole derivative (N-butyl-3,6-dibromocarbazole) in the presence of Ni[COD]$_2$ (Fig. 4a) in a satisfactory yield (18.4%). A series of molecular recognition experiments in conjunction with crystal structure analysis and theoretically simulation suggest that
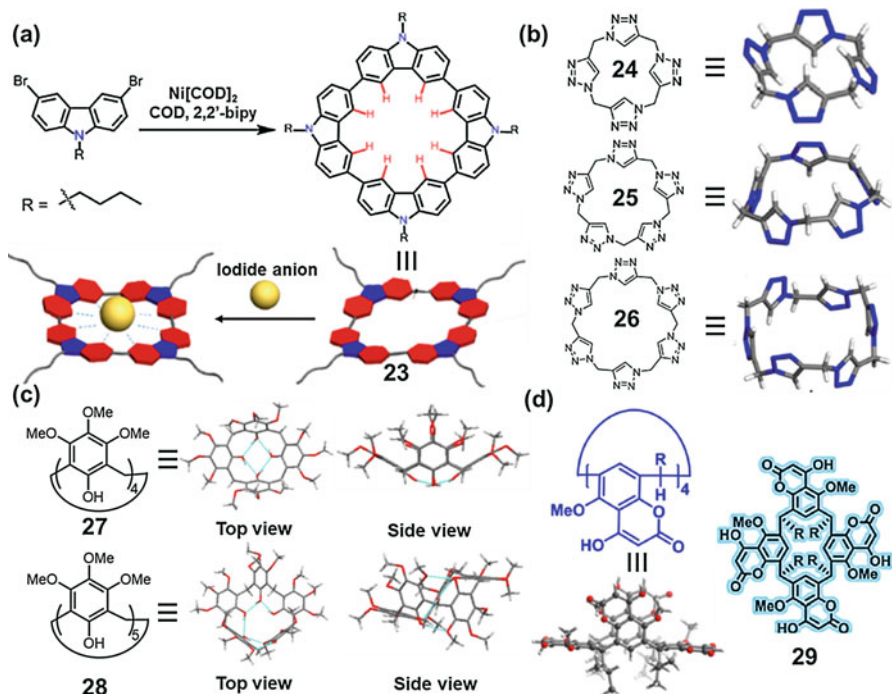
Fig. 4 (**a**) The synthetic route to cyclo[4]carbazole (**23**) and the host-guest interaction between **23** and iodide anion [45]; (**b**) the chemical and single crystal structures of calix[4,5]triazoles (**24** and **25**) as well as the simulated structure of calix[6]triazole **26** [46]; (**c**) the single crystal structures of calix[4,5]tetrolarene (**27** and **28**) [47]; (**d**) the chemical structure and single crystal structure of coumarin[4]arene (**29**) [48]

23 is a preorganized receptor for iodide ion loading, and a medium association constant of 81.8 M^{-1} obtained by UV-vis titration method is also reasonable for this kind of electron-rich macrocyclic compounds. Therefore, taking advantage of the high selectivity toward iodide anion, **23** will exert a significant influence on the sensing and removal of iodide anion.

7.2.7 Calix[n]triazoles

Calix[n]triazoles as a new category of calixarene derivatives were developed by Kim and coworkers in 2017 [46]. Calix[4–6]triazole (**24**, **25**, **26**) possessing four, five, and six triazole units could be obtained by a series of inter−/intramolecular copper (I)-catalyzed azide−alkyne cycloaddition (CuAAC) reaction (Fig. 4b). Multiple conformations of calix[n]triazoles were demonstrated by a series of conformational analyses, and the 1,3-alternate (for **24**), 1,3-alternate (for **25**), and 1,3,5-alternate (for **26**) conformers are the most stable ones according to the density functional theory

(DFT) calculations. The multi-conformational feature of calix[n]triazoles endows this group of calixarene derivatives with great potential in anion binding and molecular recognition.

7.2.8 Calix[n]tetrolarenes

Calix[n]tetrolarenes, a new family of macrocyclic arenes, were firstly reported by Cohen and Zafrani in 2017 [47]. Calix[4,5]tetrolarenes (**27**, **28**) were facilely prepared by reaction of the partially methylated 1,2,3,5-benzenetetrol and paraformaldehyde catalyzed by trifluoroacetic acid (TFA) with a total separation yield of 73% (Fig. 4c). Solvents, reaction time, temperatures, and monomeric hydroxyl groups all strongly affect the reaction rate and the distribution of products. It is noteworthy that cyclic pentamers could be facilely produced during the macrocyclization of calix[n]tetrolarenes, which has been proven to be very difficult in the synthesis of traditional calixarenes as a result of its poor thermodynamic favor. Overall, taking both advantages of the synthetic ease and fancy structures of calix[n] tetrolarenes, a wide scope of applications will be unearthed in the near future.

7.2.9 Coumarin[4]arene

In 2018, Venkatakrishnan and coworkers introduced a bicyclic heteroaromatic macrocyclic receptor, namely, coumarin[4]arene (**29**) [48]. This new macrocyclic arene, closely related to both calix[4]arene and resorcin[4]arene, meanwhile, possesses a specific fluorescence emissive property. **29** could be obtained through a two-step synthetic strategy by using easily available raw materials, giving the desirable compound in a satisfied yield of 84%. Interestingly, compared with an averaged crown conformation of **29** in solution, a stable boat conformation in the solid state was further demonstrated by X-ray single crystal diffraction (Fig. 4d). The flexibility of the structure and connatural fluorescence feature endow **29** with great potentials in molecular recognition and fluorescence sensing. For instance, the idea of constructing fluorescent capsules based on this macrocyclic arene is probable to be realized via complementary multipoint interactions in the near future.

7.3   New Macrocyclic Arenes Related to Pillarenes

7.3.1   Asararenes

In 2013, Stoddart and coworkers reported a new class of macrocyclic arenes with 6–12 aromatic units, namely, asar[n]arenes [49]. Similar to pillarenes, asar[6–15] arenes (**30–35**) could be obtained through a one-step method by reaction of the monomers (1,2,4,5-tetramethoxybenzenes) with paraformaldehyde, using $BF_3 \cdot OEt_2$ as the catalyst. Besides that, asar[6]arene (**30**) was demonstrated to be the smallest

and the thermodynamically favorable cyclic oligomer during the ring closure process. Additionally, according to the single crystal analyses, cavities of asar[6–8] arenes are occupied by its own OMe groups, while asar[9,10]arenes possess larger cavities with extra solvent molecules inside. Moreover, all the structures of asar[n] arenes in some way are analogous to the cycloalkane with the corresponding alkyne units (Fig. 5a, b). Thus, asar[n]arenes with varying sizes and shapes are highly complementary to the toolbox of supramolecular chemistry and will find a wide range of applications in host-guest chemistry and other related fields.

7.3.2 Biphenarenes

Biphen[n]arenes, a new class of macrocyclic arenes closely related to pillarenes, were first introduced by Li and coworkers in 2015 [50]. Per-ethylated biphen[3,4] arenes (**36**, **37**) could be easily synthesized by reaction of 4,4-biphenol diethyl ether building block with paraformaldehyde catalyzed by $BF_3 \cdot O(Et)_2$, giving the target products in a reasonable yield of 22% (for **36**) and 8% (for **37**) (Fig. 5c). In addition, single crystal structure of **36** exhibits a distorted triangular prism conformation, and **37** shows a "partial chair" topology conformation with the π-electron-rich cavity.
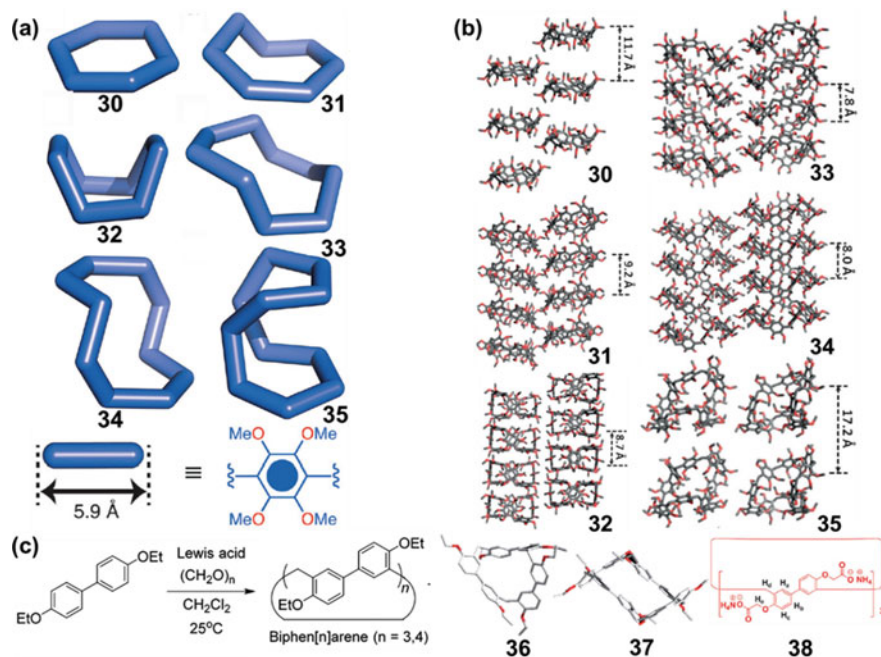

Fig. 5 (**a**) The backbones of asar[n]arenes **30**–**35** in the solid states form a variety of different shapes [49]; (**b**) side views of the crystal packing structures of **30**–**35** [49]; (**c**) the synthetic route to biphen[n]arenes (**36** and **37**) and their crystal structures and the general chemical structure of **38** [50, 52]

In addition, **36** and **37** could be deprotected by reaction with excess BBr$_3$, indicating the facile functionalization of biphen[n]arene's family. As for molecular recognition properties of biphen[n]arenes, **37** exhibits preeminent guest-friendly property and is capable of interacting with not only cationic guests but also neutral species. Furthermore, the molecular recognition properties of hydroxylated biphen[4]arene toward 2,7-dibutyldiazapyrenium and some other guests were also investigated in their following work [51].

In 2015, the first water-soluble biphen[3]arene, i.e., carboxylated biphen[3]arene (**38**), was introduced by Huang and coworkers, and meanwhile, a new supramolecular amphiphilic assembly of **38** and 1-cetylethylammonium chloride was successfully constructed [52]. Similarly, Yu and coworkers synthesized the first cationic water-soluble biphen[3]arene in 2016, which was further used to alter the aggregation behavior of the amphiphilic guest (sodium 1-hexanesulfonate) in water [53]. Very recently, Li and coworkers successfully designed and synthesized a new family of biphen[n]arenes derivatives, namely, 2,2-biphen[n]arenes [54]. Compared to the traditional biphenarenes (4,4′-biphen[n]arenes), 2,2′-biphen[n]arenes possess a higher total synthetic yield. Meanwhile, not only cyclic tetramers, high-order macrocycles including cyclic pentamers, hexamers, heptamers, and octamers were also easily synthesized and separated.

7.3.3 Cyanostar

Cyanostar (**40**), a C$_5$-symmetric star-shaped macrocycle, was first introduced by Flood and coworkers in 2013 [55, 56]. **40** could be obtained through a one-step Knoevenagel self-condensation by reaction of the meta-substituted difunctional phenylene (**39**) in a good yield of 81% (Fig. 6a). In the crystalloid state, **40** prefers to stay as π-stacked dimers constituted of chiral P and M enantiomers (Fig. 6c). In the solution, **40** exhibits outstanding binding properties toward PF$_6^-$, BF$_4^-$, and ClO$_4^-$, endowing **40** with great potentials in the detection and separation of electronegative species. Moreover, owning to its anionic preference and shape-persistent features, a phosphate-templated [3]rotaxane could be synthesized in a high yield through click chemistry (Fig. 6b). The efficient synthetic step cooperates with the outstanding ionic recognition property bringing cyanostar all kinds of applications in supramolecular chemistry and other related fields [57–59].

7.3.4 Campestarenes

Campestarenes (**41**–**44**), a family of modifiable macrocycles based on Schiff base, were first introduced by MacLachlan and coworkers in 2011 [60]. Hydroxyl groups in this fivefold symmetrical macrocycle guaranteed its flat conformation and stabilized the imine moieties via hydrogen bond interactions (Fig. 7a). Theoretical calculation of **44** demonstrated that an enol-imine tautomeric state is predominant in the gas phase or nonpolar solvents, while a keto-enamine tautomeric state is
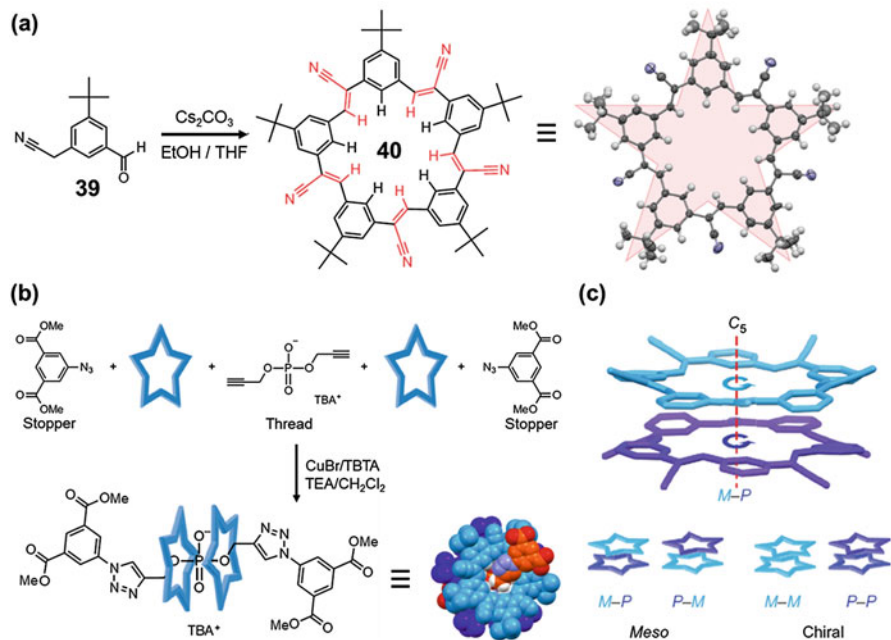
Fig. 6 (**a**) Synthetic route to cyanostar (**40**) and its single crystal structure [55]; (**b**) synthetic scheme for the phosphate-templated [3]rotaxane and its Corey-Pauling-Koltun (CPK) model [55]; (**c**) sandwiches of two bowl-shaped cyanostars result in a mixture of four possible stereoisomers [55]

dominant in the polar solvents. Then, **45** was successfully synthesized by the same group in 2016 [61]. Similarly, the initial single crystal of **45** also exhibits a flat conformation, and only enol-imine tautomer exists in nonpolar solvents (Fig. 7b). Recently, campestarenes bearing functional moieties were first designed and synthesized by Brothers and coworkers in 2018 and, indeed, extended the application fields of campestarene family [62]. Meanwhile, by introducing the ranyl(VI) as the template, MacLachlan and coworkers discovered two expanded version of campestarenes with six (**46**) or eight (**47**) repeating units, definitely, and their electron-rich features guarantee a wide range of supramolecular functions to be exploited in the near future (Fig. 7c) [63].

7.3.5 Oxatub[n]arenes

Oxatub[4]arene (**48**), a macrocyclic receptor with multiple interconvertible cavities, was first introduced by Jiang and coworkers in 2015 [64]. **48** was synthesized in a reasonable yield of 21% through the well-known Williamson ether condensation by reaction of 2,6-dihydroxynaphthalene and 2,6-dibromonaphthalene under a high-dilution condition (Fig. 8a). Meanwhile, the intriguing structure endows **48** with
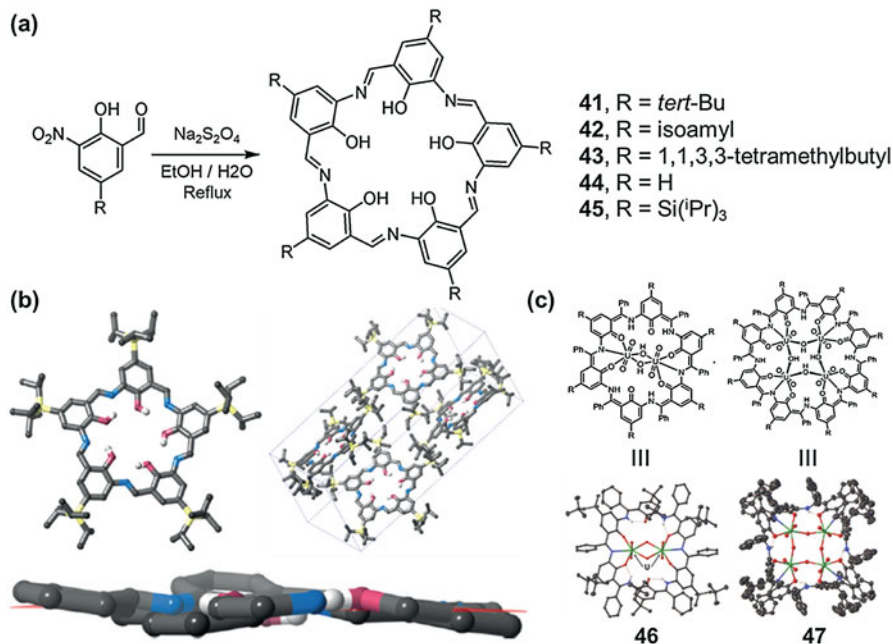
Fig. 7 (**a**) Synthetic route to campestarenes (**41–45**) [60, 61]; (**b**) different modes of single crystal structure of **45** [61]; (**c**) general chemical structures and single crystal structures of **46** and **47** [63]

specific features including lower steric hindrance between neighboring units, straightforward and facile synthesis, and no self-occupied cavity (Fig. 8b). Definitely, the single crystal analyses in conjunction with the ^{1}H NMR, 2D NMR experiments demonstrated four representative conformations that are interconvertible in **48**. In other words, the conformation changed predictably due to the structural difference of certain guests being applied (Fig. 8c). Similarly, oxatub[5,6]arenes (**49, 50**) with larger cavity size and more interconvertible conformations were reported by the same group in 2017 (Fig. 8a) [65]. Due to the larger cavity size, **50** exhibited a nice binding affinity toward both C_{60} and C_{70} (216 M^{-1} for C_{60} and 548 M^{-1} for C_{70}). Thus, the diversiform and flexibility of oxatub[n]arenes indicate its wide application in different host-guest systems.

7.3.6 [m]Biphenyl-Extended Pillar[n]arenes

Macrocyclic arenes with large cavity size are always obtained in poor synthetic yields [22, 24]. In order to conquer this challenge, [m]biphenyl-extended pillar [n]arenes ([m]Bp-ExPns) were successfully designed and prepared by our group in 2016 [66]. [m]Bp-ExPns with rigid backbone and large cavity size were facilely synthesized by a two-step strategy. Firstly, pre-connection of the
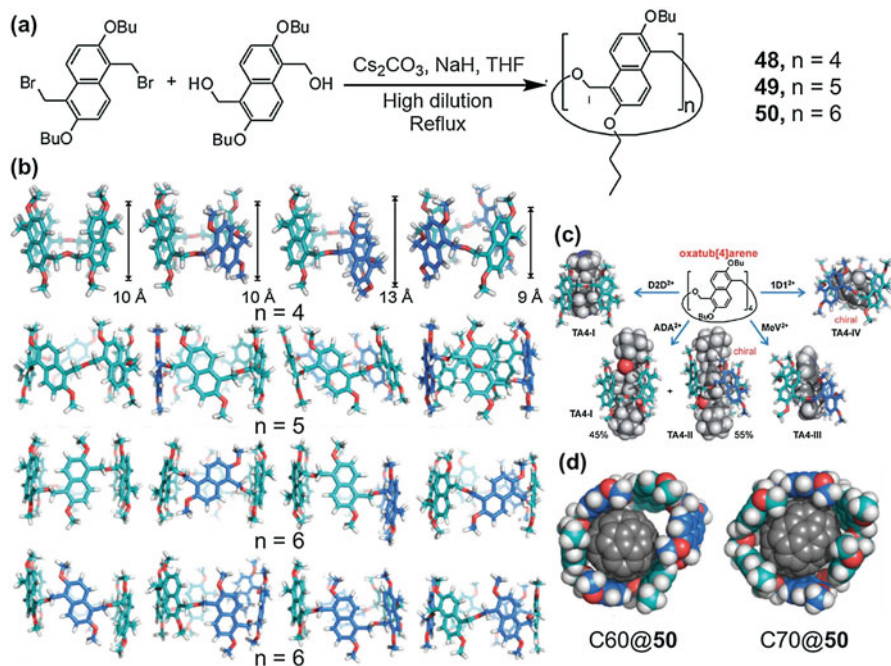
Fig. 8 (**a**) The synthetic route to oxatub[4]arenes (**48–50**) [64]; (**b**) chemical structures of four representative conformers of **48**, **49**, and **50** resulting from naphthalene flipping [64]; (**c**) summary of guest-selected predominance of one of the four conformers of **48**. Butyl groups in the models were abbreviated to methyl groups for viewing clarity [64]; (**d**) energy-minimized structures of C_{60}@**50** and C_{70}@**50** [65]

1,4-dimethoxybenzene with diphenyl under Friedel-Crafts alkylation reaction gave the intermediate product (MDM) in a good yield of 50%. Secondly, via the direct condensation of MDM with paraformaldehyde in the presence of $BF_3 \cdot O(Et)_2$, [2] Bp-ExP6 (**51**), [3]Bp-ExP9 (**52**), [2]Bp-ExP5 (**53**), and [2]Bp-ExP7 (**54**) could be successfully synthesized and separated with yields of 50%, 1.2%, 0.1%, and 0.1%, respectively (Fig. 9a). The main product [2]Bp-ExP6 (**51**) could be considered as an extended version of traditional pillar[6]arene with the replacement of two opposite 1,4-dimethoxybenzene units by biphenyl units; both the synthetic yield and cavity size are enhanced evidently. Importantly, the single crystal structures of **51** bearing toluene or m-xylene molecule impart **51** with promising potentials in petrochemical field. Very recently, the first water-soluble [2]Bp-ExP6 (**55**) bearing eight pyridinium moieties was successfully designed and synthesized, which exhibited outstanding binding affinity toward certain sulfonate species in virtue of its distinctive cavity size and positively charged feature [67]. More importantly, 2,6-naphthalene-disulfonate could be easily captured and separated by **55** from its aqueous solution in a form of coprecipitation, which endows **55** with unlimited potentials in the separation and detection of sulfonate species in water (Fig. 9c).
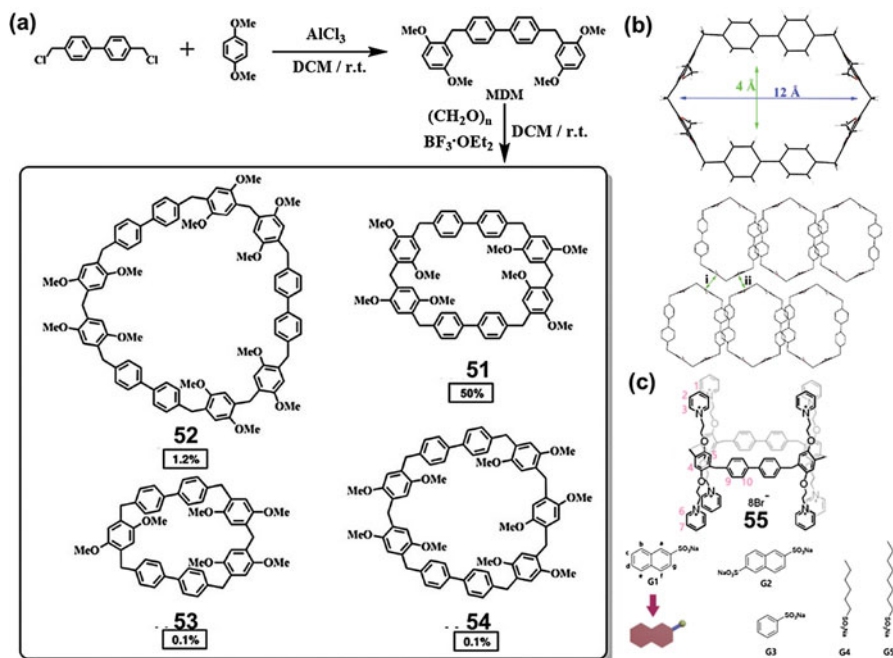
Fig. 9 (**a**) Synthetic route to biphenyl-extended pillarenes (**51–54**) [66]; (**b**) crystal structures of [2] Bp-ExP6 (**51**) [66]; (**c**) the chemical structure of the water-soluble [2]Bp-ExP6 (**55**) and the selected sulfonate guests related to **55** [67]

7.3.7 Pillar[4]pyridinium

A highly symmetric and quadrupled positively charged macrocycle, namely, pillar [4]pyridinium (**56**), was introduced by Sashuk, Szumna, and coworkers in 2017 [68]. **56** could be produced by condensation of 4-(bromomethyl) pyridine hydrobromide with equimolar amounts of $NaHCO_3$ and NH_4PF_6 in acetonitrile (Fig. 10a), giving the target product in a good yield of 50%. Significantly, similar to calix[n]imidazolium as aforementioned, **56** could also serve as an effective fluoride receptor in aqueous solution. In a word, taking advantage of the electron-rich feature, pillar[4]pyridinium will find a wide range of applications in the field of ion sensing.

7.3.8 Leaning Pillar[6]arenes

Very recently, a new version of pillar[6]arenes with desirable cavity adaptability and enhanced guest-binding capability, namely, leaning pillar[6]arenes (or leaning towerarenes), was first reported by our group [69–71]. The synthesis of leaning pillar[6]arenes was accomplished by a facile two-step synthetic approach including
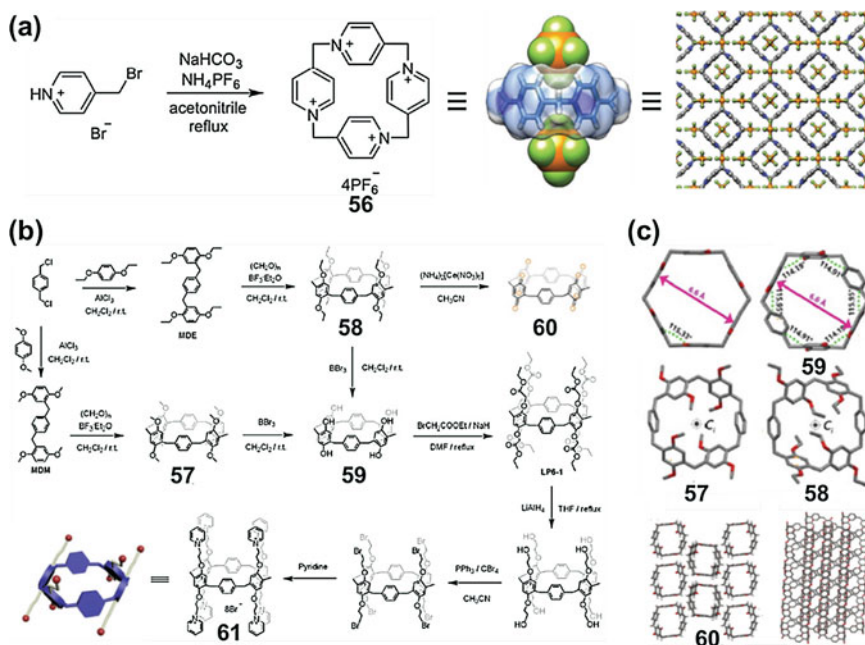
Fig. 10 (**a**) The synthetic route to pillar[4]pyridinium (**56**), the ion pairing between **56** and two PF$_6^-$ anions, and the crystal packing of **56** viewed from the a direction [68]; (**b**) synthetic route to leaning towerarenes (**57–61**) [69]; (**c**) the single crystal structures of pillar[6]arene and leaning pillar [6]arenes (**57–60**) [69]

a Friedel–Crafts alkylation reaction in conjunction with the Lewis acid catalyzed macrocyclization reaction, giving the MeLP6 and EtLP6 (**57, 58**) in a reasonable yield of >30%, respectively (Fig. 10b). Significantly, the single crystal analyses in coordination with DFT calculation gave a simple and intuitive explanation for the pillarenes prefer to maintain a pillar-like and rigid structure. Meanwhile, the same synthesis strategy may apply in other pillarenes as well as other macrocyclic arene systems, especially those with mediocre synthetic yields.

It is well known that the modification of macrocyclic receptors by introducing various functional groups can provide numerous categories of interesting properties. As in Fig. 10b, by cleavage of the ether groups in **57** or **58,** per-hydroxylated leaning pillar[6]arenes (**59**) could be quantitatively produced. Immediately, a series of functionalized leaning pillar[6]arene derivatives especially a water-soluble version (**61**) were facilely designed and synthesized. Significantly, the presence of eight positive pyridinium moieties made the **61** an effective anion receptor. In brief, a tilted conformation rather than a traditional pillar structure endows the leaning towerarenes with great performance in macrocyclic and supramolecular chemistry.

7.4   Concluding Remarks

In summary, recent advances in synthetic macrocyclic arenes closely related to calixarenes and pillarenes have been highlighted in this chapter. These macrocycles include calix[2]arene[2]triazines, calix[n]imidazoliums, TPE-based oxacalixarenes, hybrid[n]arenes, calix[3]carbazole, cyclo[4]carbazole, calix[n]triazoles, calix[n] tetrarenes, coumarin[4]arene, asararenes, biphenarenes, cyanostars, campestarenes, oxatub[n]arenes, biphenyl-extended pillarenes, pillar[4]pyridinium, and leaning towerarenes. Although most of the current researches still center on the structural design and synthetic methodology, the research on their variety of functions is still yet to be exploited. But, all of them will certainly enrich the toolbox of supramolecular macrocyclic chemistry and indeed unleash new opportunities in future supramolecular chemistry research. In our lab, we are now in the processes of functionalizing the extended pillarenes for detection of environmentally harmful ions and modifying leaning pillar[6]arenes to obtain stimuli-responsive supramolecular polymers and smart hybrid nanomaterials. In any event, for gaining broad attention by researchers, synthetic macrocycles should at least possess features as follows: (i) easy accessibility and low price, (ii) unique geometries, (iii) special and selective binding properties, and (iv) ease of modification. We strongly believe that all the macrocyclic arenes covered in this chapter possess unlimited potentials and great possibilities in finding more and more applications.

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