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REVIEW PAPER

Synthesis of novel pillar-shaped cavitands "Pillar[5]arenes" and their application for supramolecular materials

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Abstract In 2008, we reported a new class of macrocyclic hosts and named "Pillar[5]arenes". They combine the advantages and aspects of traditional hosts and have a composition similar to those of typical calix[*n*]arenes. Pillar[5]arenes have repeating units connected by methylene bridges at the *para*-position, and thus they have a unique symmetrical pillar architecture differing from the basket-shaped structure of *meta*-bridged calix[*n*]arenes. Pillar[5]arenes show high functionality similar to cyclodextrins, and can capture electron accepting guest molecules within their cavity similarly to cucurbit[*n*]urils. In this review, the synthesis, structure, rotation, host–guest properties, planar chirality and functionality of pillar[5]arenes are discussed, along with pillar[5]arene-based supramolecular architectures and the challenges in synthesizing pillar[6]arenes.

Keywords Pillar[5]arene · Host–guest complex · Polyrotaxane · Planar chirality · Functionality

Introduction

Macrocyclic compounds have attracted considerable attention because of their interesting structural features.

(1) Unlike linear structures, macrocyclic structures have no terminal groups, and thus highly symmetric architectures are expected.
(2) In contrast to low and high molecular weight compounds, the molecular weight of macrocyclic compounds range from several hundred to in the thousands, and they exhibit interesting properties depending on the oligomers molecular weight.
(3) The typical size of a macrocyclic compound is approximately 1 nm. Interesting supramolecular assemblies on the nanometer scale can be constructed by the building up of nano-scale macrocyclic compounds.
(4) They can capture guest molecules in their vacant cavity via various physical interactions.

Due to their structure, molecular weight and size, macrocyclic compounds play a major role as host molecules and building blocks for the construction of supramolecular architectures including catenanes [1–3], rotaxanes [4–6], polycatenanes [7–9], polyrotaxanes [10] and topological gels [11, 12].

Cyclodextrins (CDs), crown ethers and *meta*-bridged cyclophane derivatives (calix[*n*]arenes) are well-known classical macrocyclic compounds, with the former having the longest research history [13–15]. CDs can be obtained from natural products and their structure was first reported in 1903 by F. Schardinger. Crown ethers were the first synthetic macrocyclic compounds, and were first reported by Pedersen in 1967 [16–18]. In 1978, phenolic macrocycles calix[*n*]arenes were reported by Gutsche [19–22]. Much subsequent attention has been paid to the design of new macrocyclic hosts, which have been synthesized by ring closure reactions such as palladium- and copper-mediated coupling [23–28], Diels-Alder [29], formation of amide [30, 31], ester [32] and ether bridges [33]. Among

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them, cucurbit[*n*]urils are an example, which shows interesting host–guest properties resulting from their symmetrical pumpkin-shaped architecture [34–39]. In 1981, cucurbit[6]uril was fully characterized by Mock [34], and in early 2000, Kim reported the synthesis and isolation of cucurbit[*n*]uril homologues containing different numbers of glycol units, and cucurbit[*n*]uril derivatives that were soluble in common solvents [35]. Due to their highly symmetrical architectures, they form very stable host–guest complexes with organic and inorganic cations, and with neutral organic guests in aqueous media. The design and synthesis of new macrocyclic molecules intimately led to further developments in host–guest and supramolecular chemistry. Improvements in analytical tools such as scanning electron microscopy (SEM), transmittance electron microscopy (TEM), atomic force microscopy (AFM) and scanning tunneling microscopy (STM) have also accelerated such research. Under favorable conditions, macrocyclic molecules and supramolecular assemblies can be directly observed with such tools [40–43].

Some of the most significant problems in the synthesis of new macrocyclic hosts are the low yields and cumbersome synthetic pathways. For example, even in optimized conditions, yields for isolated cucurbit[*n*]urils are 8% ($n = 5$), 46% ($n = 6$), 24% ($n = 7$) and 8% ($n = 8$) [39]. Improving yield and the development of convenient synthetic procedures for these macrocyclic hosts are necessary for them to become more widely accepted and utilized.

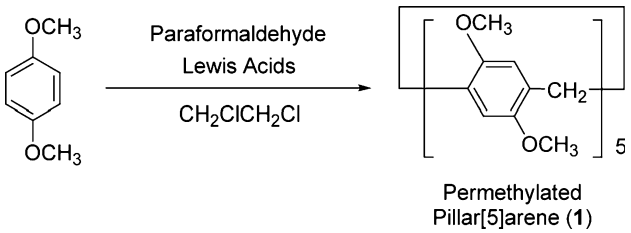
In 2008, we reported a new class of macrocyclic hosts named "Pillar[5]arenes" [44]. The key compound permethylated pillar[5]arene can be obtained in a high yield from a one-step reaction [45]. In this review, the synthesis, structure, rotation, host–guest properties, planar chirality and functionality of pillar[5]arenes are discussed, along with pillar[5]arene supramolecular architectures, and challenges in the synthesis of pillar[6]arenes.

Permethylated and perhydroxylated pillar[5]arenes: synthesis, structure and physical properties

Synthesis

The reaction of phenolic compounds with aldehydes affords calix[*n*]arenes [19–22], and similar reagents are used for the synthesis of permethylated pillar[5]arene (**1**) as shown in Scheme 1 (in this case 1,4-dimethoxybenzene with paraformaldehyde).

The difference in synthesis pathway between calix[*n*]arenes and pillar[5]arenes is the reaction conditions. Calix[*n*]arenes are generally obtained from the base-catalyzed condensation of a phenolic derivative and formaldehyde, while **1** is effectively obtained using an



Scheme 1 Synthesis of permethylated pillar[5]arene (**1**)

appropriate Lewis acid [44]. Figure 1 shows size-exclusion chromatography (SEC) using various Lewis acids. Using inappropriate Lewis acids such as aluminium(III) chloride, iron(III) chloride, titanium(IV) chloride and tin(IV) chloride yields a mixture of polymer and **1** (Fig. 1a). In contrast, using boron trifluoride diethyl etherate [$BF_3{\cdot}O(C_2H_5)_2$] (Fig. 1b) selectively yields **1** in a 22% yield. To determine the ideal conditions for the synthesis of **1**, we monitored the cyclization reaction using SEC profiles of the product at various times. After adding $BF_3{\cdot}O(C_2H_5)_2$, the 1,4-dimethoxybenzene peak dramatically decreased and the peak due to **1**, indicating that the reaction quickly took place. Over 180 s, the SEC traces hardly changed, which indicates completion of the cyclization reaction. We also investigated the effect of paraformaldehyde quantity on the cyclization. Using 0.2 and 0.33 eq. of paraformaldehyde per eq. of 1,4-dimethoxybenzene afforded a mixture of 1,4-dimethoxybenzene-end oligomers and **1**. The product from 1.0 eq. of paraformaldehyde contained **1** and polymer, and excess paraformaldehyde (3.0 and 5.0 eq.) led to the peak solely due to **1**. Using excess paraformaldehyde was expected to result in formation of methylol-end oligomers which are reactive and converge to **1**. We concluded that a 30 min reaction using 3 eq. of paraformaldehyde was the optimum condition for the synthesis of **1** [45]. Pure **1** was isolated from the reaction mixture by the addition of methanol, collection of the precipitate, and removal of insoluble species with chloroform. The obtained solid was re-crystallized from chloroform/acetone (1:1 v/v) to yield crystalline **1** (Yield: 71%), which was assigned as a *para*-bridged cyclophane derivative. Synthesis of *para*-bridged cyclophane derivatives is difficult in contrast to various *ortho*- and *meta*-bridged cyclophane derivatives which have been reported. The synthesis of the *para*-bridged [1.1.1.1.1]cyclophane was reported more than 20 years ago, however, its synthesis is laborious and the overall yield is below 1% [46]. Connections between *para*-substituted units afford rigid linear oligomers in comparison with *ortho*- and *meta*-substituted monomers, and *intra*-molecular cyclization should be minimal. **1** is a strain-free structure, and thus **1** is obtained selectively in a high yield (Detail conformational structure of **1** is described in the next section). We used

commercially available 1,4-dimethoxybenzene, paraformaldehyde and $BF_3{\cdot}O(C_2H_5)_2$ for the synthesis of **1**. The short reaction time and recrystallization led to **1** in a high yield. Permethylated pillar[5]arene **1** is a useful building block in host–guest and supramolecular chemistry, and our procedure allows for its large scale synthesis.

Using appropriate Lewis acids led to **1** being selectively obtained, and the use of Lewis acids for calix[*n*]arene and calix[*n*]resorcinarene synthesis has also been examined [47–49]. By using $BF_3{\cdot}O(C_2H_5)_2$, the condensation of 1,2- and 1,3-dimethoxybenzene produced cyclotriveratrylene (**2**, Scheme 2a) and octamethoxycalix[4]resorcinarene (**3**, Scheme 2b), respectively. The condensation of 1,3,5-trimethoxybenzene with paraformaldehyde under $BF_3{\cdot}O(C_2H_5)_2$ yielded the first dodecamethoxysubstituted calix[4]arene (**4**, Scheme 2c) [47]. The $BF_3{\cdot}O(C_2H_5)_2$ catalyzed condensation of 3-methoxyphenol with octanal produced the *C4* symmetric calix[4]resorcinarene in a high yield (**5**, Scheme 2d) [48]. Thus, Lewis acids are useful reagents for the synthesis of the phenolic macrocyclic hosts.

The de-protection of the methoxy-substituents of **1** has also been investigated. The reaction of **1** with BBr_3 in anhydrous chloroform afforded perhydroxylated pillar[5]arene (**6**, Scheme 3).

Structure and physical properties

The structures of permethylated (**1**) and perhydroxylated pillar[5]arenes (**6**) have been fully characterized by using spectroscopic methods and X-ray crystallography (Fig. 2) [44, 45]. The structure of **1** is a cyclic pentamer of 1,4-dimethoxybenzene units in **1** connected by methylene bridges at the 2 and 5 positions (Fig. 2b). The structure of **1** appears as an equilateral pentagon from above (Fig. 2a) and as symmetrical pillars from the side (Fig. 2b). The methylene bridge linkages at the 2 and 5 positions of the benzene ring result in the interesting symmetrical structure, in contrast to typical calix[*n*]arenes forming vase-shaped architectures due to methylene bridges at their *meta*-position. Therefore, the structure of **1** is different from that of typical calix[*n*]arenes. The average methylene bridge angle between the units in **1** is approximately 110° (Fig. 2a), similar to the stable single C–C–C bond angle of 109.5°. Therefore, **1** is a conformationally stable macrocyclic compound. The low strain energy means that **1** can be obtained in a high yield, and X-ray crystal structures revealed that acetonitrile was included in the cavity. The diameter of the cavity is approximately 5 Å, which is almost analogous to that of α-CD [50]. Similar to **1**, the structure of perhydroxylated pillar[5]arene (**6**) is a cyclic pentamer with constituent units connected by methylene bridges at the *para*-position (Fig. 2d). Two acetone molecules were included in the cavity, and *intra*-molecular hydrogen bonds between OH groups were observed in contrast to the structure of **1**. *Inter*-molecular hydrogen bonds of OH groups with OH moieties in the other perhydroxylated pillar[5]arene molecules and with the carbonyl groups in two acetone molecules were also found. Such *intra*- and *inter*-molecular hydrogen bonds disturb the pentagonal structure (Fig. 2c, top view) and induce twisting of the constituent units (Fig. 2d, side view). In a solid state, the twisting of two phenolic units (Fig. 2f, 1 and 3 positions) in **6** was observed, whereas no twisting of units took place in **1** (Fig. 2e). Twisting was not reported in the X-ray analysis of the other peralkylated pillar[5]arenes, and is a specific property of the perhydroxylated pillar[5]arene **6**.

Figure 3 shows the ^{1}H NMR spectra of **1** and **6**, in which proton signals appear as singlets. In typical calix[*n*]arenes, proton signals are split since they are nonsymmetric structures, so these methylene and benzene protons are easily distinguishable [19–22]. The ^{1}H NMR spectra of these pillar[5]arenes imply highly symmetrical structures.

Permethylated pillar[5]arene **1** is soluble in organic solvents including chloroform, acetone, acetonitrile, THF, DMF and DMSO, whereas perhydroxylated pillar[5]arene **6** is soluble in acetone, acetonitrile, THF, methanol, DMF, DMSO and a basic aqueous solution. The deprotection of methoxy-substituents increases the polarity of pillar[5]arene, and functional groups modified on both rims significantly affect the physical properties of pillar[5]arenes.

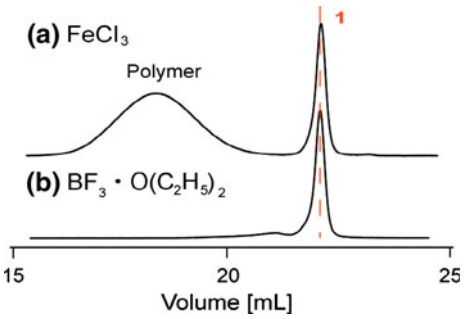
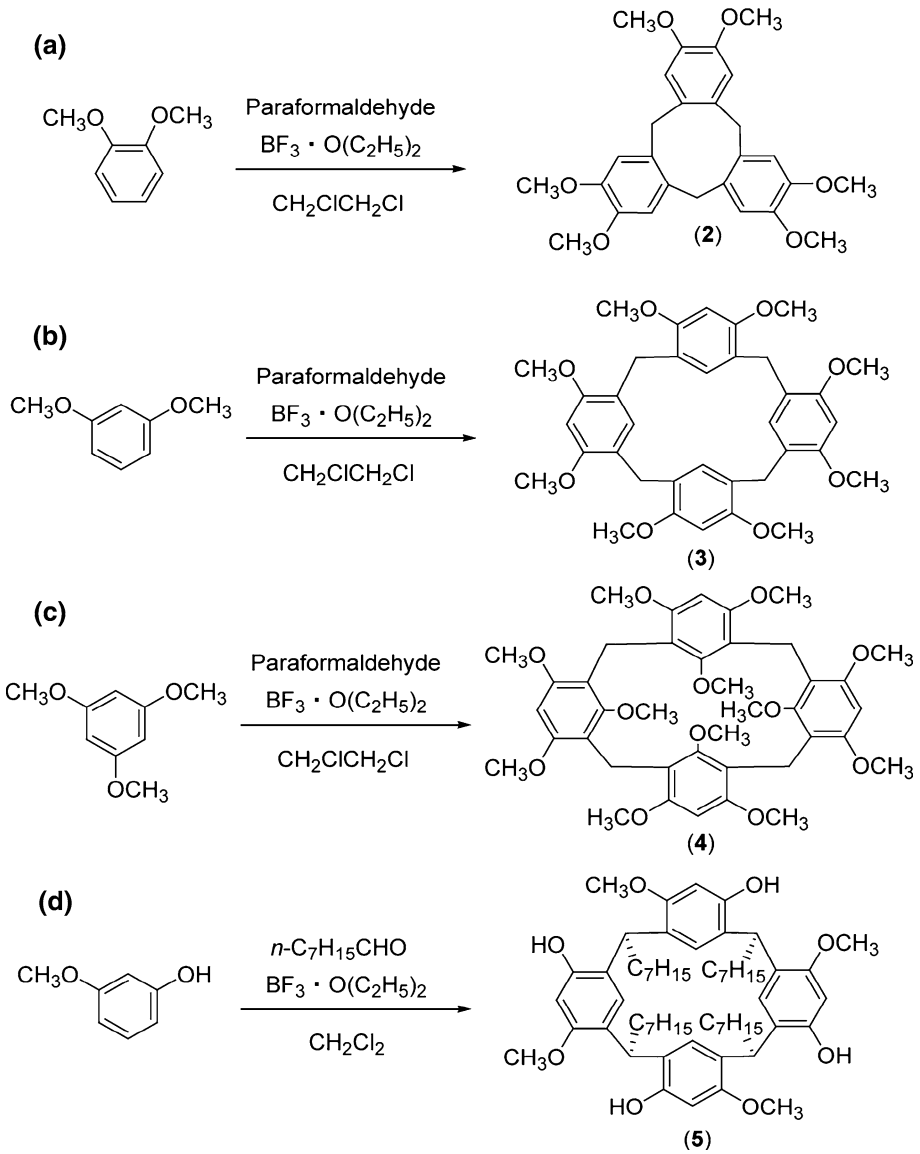


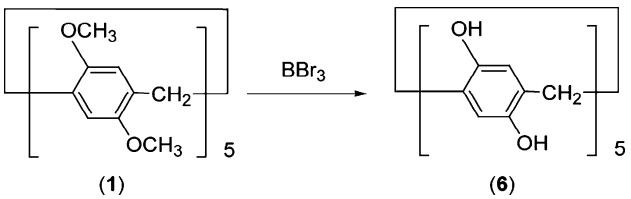
Fig. 1 SEC traces using various Lewis acids. Reprinted with permission from Ref. [44]

Pillar[5]arene and pillar[6]arene derivatives

The functionalization of pillar[5]arenes with various groups enables tuning the properties such as solubility, optical response and crystallinity, so established functionalization procedures need to be developed. For the synthesis of new pillar[5]arene derivatives, two synthetic pathways are possible: functionalization of preformed perhydroxylated pillar[5]arene **6** (Fig. 4a) and cyclization or co-cyclization of 1,4-dialkoxybenzene monomers containing alkoxy groups (Fig. 4b).



Scheme 2 Lewis acid catalyzed synthesis of *ortho*- and *meta*-bridged cyclophane derivatives from alkoxybenzene monomers



Scheme 3 Deprotection of methoxy-substituents of **1**

Functionalization of preformed perhydroxylated pillar[5]arene (Fig. 4a)

Perhydroxylated pillar[5]arene (**6**, Fig. 5) has 10 reactive OH groups similar to CDs, and modification of the OH groups can provide various perfunctionalized pillar[5]arene derivatives. Palladium catalyzed reactions such as Sonogashira, Suzuki and Heck couplings have been widely used for the synthesis of π-conjugated molecules and polymers [51–54], and as a suitable precursor for such transformation, pertriflated pillar[5]arene (**7**) has previously been prepared. The Sonogashira coupling of **7** and ethynylbenzene gave perphenylethynylated pillar[5]arene (**8**) [55]. The high symmetrical scaffold of the pillar[5]arene and low conformational mobility of **8** resulted in efficient through-space π-delocalization within the cavity. Repeating π-conjugated units were largely π-delocalized via through-space within the cavity, and **8** exhibited temperature- and solvent-responsive blue-green emission. The etherification of **6** with functional groups is also a relatively straightforward approach, with percyclohexylmethylated (**9**) [56], percyclohexylethylated (**10**) [56] and perethoxycarbonylmethylated pillar[5]arenes (**11**) [57] all having been synthesized. The hydrolysis of **11** under basic conditions afforded the percarboxylic acid-substituted pillar[5]arene (**12**). Neutralization to the ammonium salt with

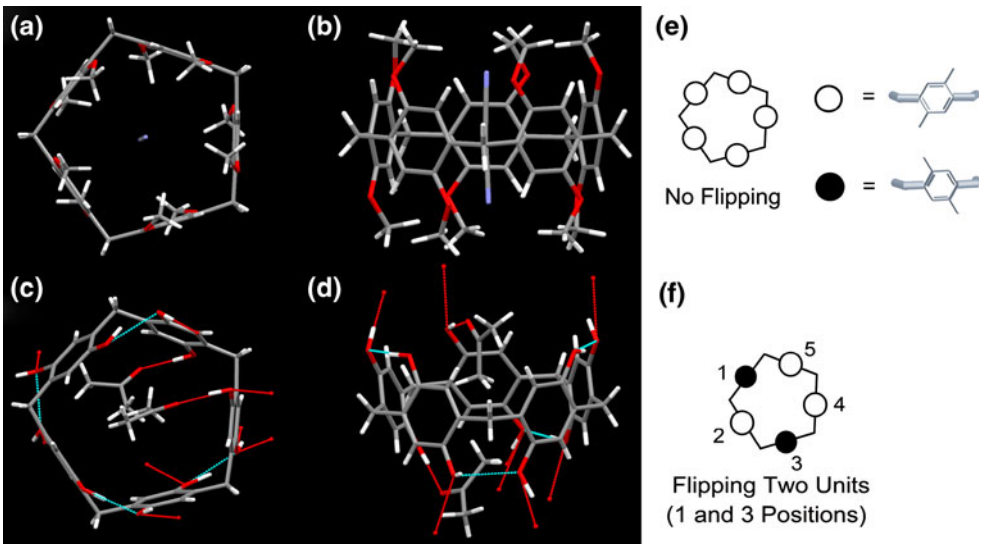


Fig. 2 X-ray crystalline structures of **a**, **b** permethylated pillar[5]arene (**1**) and **c**, **d** perhydroxylated pillar[5]arene **6** from **a**, **c** above and **b**, **d** the side views. Conformations of **e 1** and **f 6** in a crystalline state

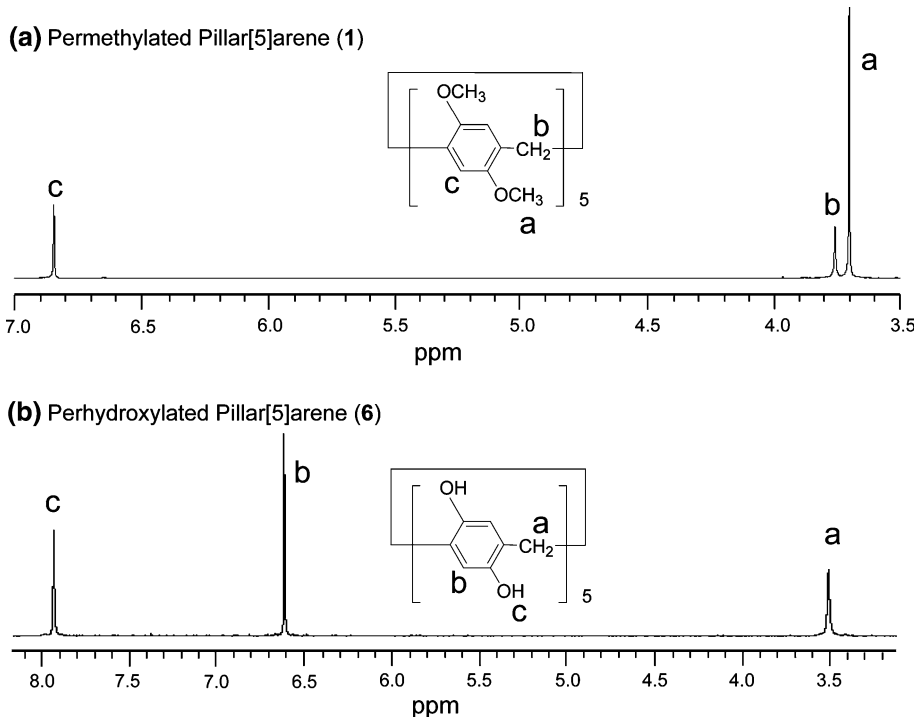


Fig. 3 ^{1}H NMR spectra of **a 1** in $CDCl_3$ and **b 6** in acetone-d_6

aqueous ammonia afforded the first water-soluble pillar[5]arene salt (**13**).

The reduction of **11** with lithium aluminum hydride gave **14**, subsequent treatment with tetrabromomethane and triphenylphosphine afforded **15**. Further reaction with sodium azide produced **16**, and finally the palladium-catalyzed hydrogenation of **16** afforded **17** [58]. Introduction of bulky substituents such as benzyl and pyrenyl groups using click reactions was also reported [59].

The monofunctionalization of pillar[5]arene has not been previously accomplished and remains an important milestone, however the modification of all 10 OH groups of pillar[5]arene to introduce further functionality has been reported. The position-selective functionalization of macrocyclic host molecules has expanded the possibilities for their application [60–64]. We reported the synthesis of mono-hydroxylated pillar[5]arene (**18**, Fig. 6) by optimizing the deprotection conditions of permethylated pillar[5]arene (**1**). The monohydroxy group in **18** is reactive and the introduction of other monofunctional groups to **18** is now possible. Thus, **18** is a useful compound for synthesizing further pillar[5]arene derivatives [65]. The first

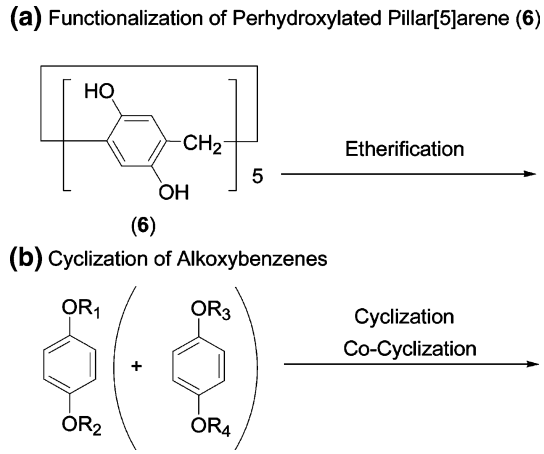


Fig. 4 Synthetic pathways for pillar[5]arene derivatives

synthesis of a di-functionalized pillar[5]arene has been carried out, by in situ cyclization and deprotection [66].

Cyclization of alkoxybenzene monomers (Fig. 4b)

The reaction of alkoxybenzene monomers afforded alkyl-substituted pillar[5]arene derivatives (Fig. 4b), but such monomers containing functional groups (except alkyl moieties) did not yield macrocyclic pillar[5]arenes. Thus, the cyclization approach is limited to the preparation of alkylated pillar[5]arenes. We synthesized a new series of

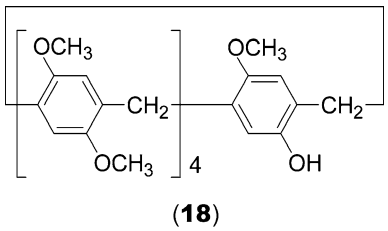


Fig. 6 Chemical structure of mono-hydroxylated pillar[5]arene (**18**)

peralkylated pillar[5]arene derivatives including perethylated pillar[5]arene (**19**), perpropylated pillar[5]arene (**20**), perbutylated pillar[5]arene (**21**), perpentylated pillar[5]arene (**22**), perhexylated pillar[5]arene (**23**) and perdodecylated pillar[5]arene (**24**, Fig. 7a) [67]. The branched alkyl-substituted pillar[5]arene (**25**) [68] and pillar[5]arene containing chiral 2-(*S*)-methylbutoxy moieties at both rims (**26**) [69] were also synthesized.

Using 1-ethoxy-4-methoxybenzene as a monomer, we synthesized nonsymmetric *penta*-ethylated-*penta*-methylated pillar[5]arene (**27**, Fig. 7b) [70], in which the ^{1}H NMR signals of the benzene, methylene bridge and alkoxy moieties were split. After that, nonsymmetric *penta*-butylated-*penta*-methylated pillar[5]arene (**28**) was also reported by Huang and Meier groups [71, 72]. Hunag and coworkers reported copillar[5]arenes. The co-cyclization of different monomers yielded pillar[5]arenes containing

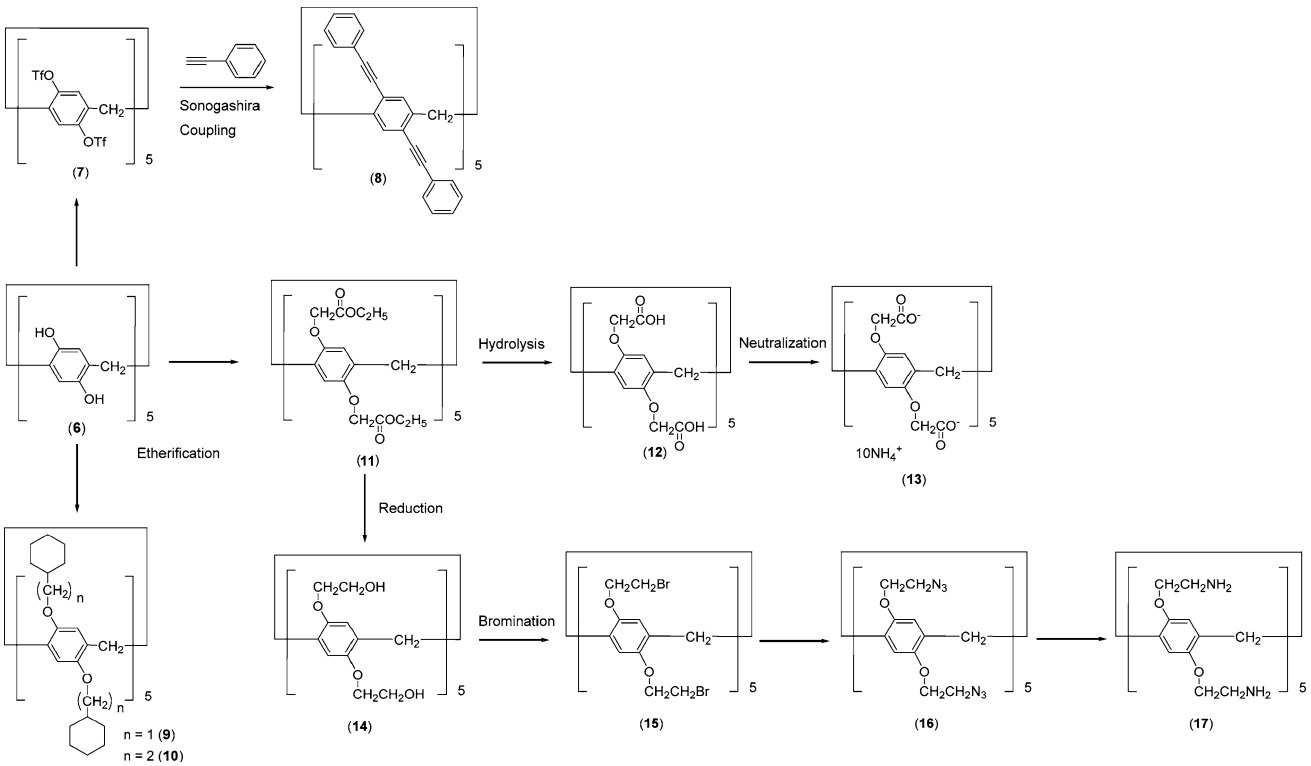


Fig. 5 Synthesis of functionalized pillar[5]arene derivatives from preformed perhydroxylated pillar[5]arene as a starting reagent

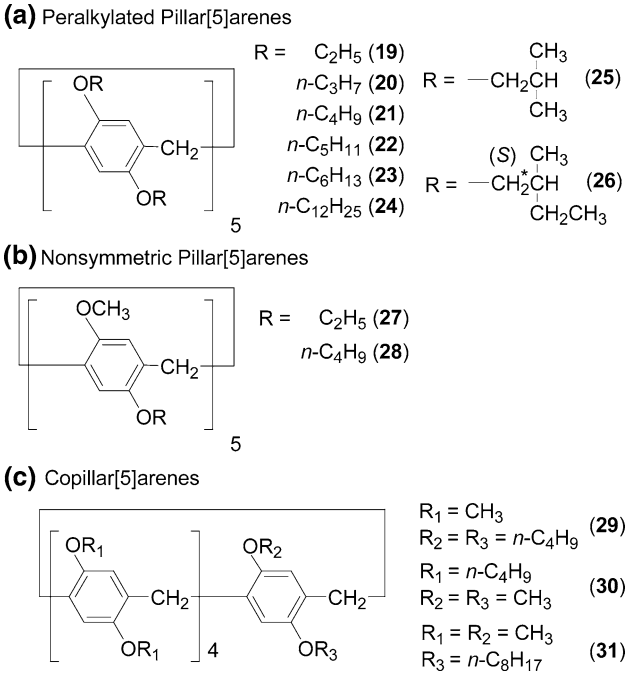


Fig. 7 Synthesis of various per-alkylated pillar[5]arenes by cyclization of 1,4-dialkoxybenzene monomers

different repeating units (Fig. 7c). Examples include those consisting of one *para*-dibutoxybenzene unit and four *para*-dimethoxybenzene units (**29**) and one *para*-dimethoxybenzene and four *para*-dibutoxybenzene units (**30**), which were prepared by co-cyclization at the appropriate ratio [73]. The co-cyclization of four eq. of 1,4-dimethoxybenzene and one eq. of 1-methoxy-4-octyloxybenzene yielded mono-octylated pillar[5]arene (**31**) [74]. The combination of different alkoxybenzene monomers is one approach for the position selective modification of pillar[5]arenes.

Synthesis of pillar[6]arenes

Expanding the synthesis of pillar[5]arene homologues into pillar[*n*]arenes will extend further this field of chemistry, similar to calix[*n*]arene [75] and cucurbit[*n*]uril [76] chemistry. The synthesis of pillar[6]arenes was reported by Meier and coworkers in 2009. However, the cyclic pentagonal structure of pillar[5]arenes is very stable, and the hexagonal structured pillar[6]arenes were obtained only as minor products. The reaction of a 1,4-dibuthoxybenzene derivative with *para*-toluenesulfonic acid afforded a mixture of perbuthylated pillar[5]arene (yield 86%) and pillar[6]arene (**33**, yield 11%, Fig. 8) [77]. The condensation of a 1,4-diisobutoxybenzene derivative and *para*-toluenesulfonic acid yielded the perisobutylated pillar[5]arene (yield 73%) and also pillar[6]arene (**34**, yield 4.6%) [68]. A single crystal X-ray structure of **34** was also reported by Huang and coworkers. Since pillar[6]arenes were obtained as minor products and their synthesis remains difficult, new synthetic procedures for their synthesis are greatly desired.

Rotational property and planar chirality of pillar[5]arenes

Calix[*n*]arenes made from phenolic units have many conformers due to the two possible rotation modes of the phenolic unit: the oxygen-through-the-annulus rotation and the *para*-substituent-through-the annulus rotation [78, 79]. The only possible rotation mode for the phenolic unit in pillar[5]arenes symmetric structure is the oxygen-through-the-annulus rotation, and the phenolic units rotate around methylene bridges as the axis. Pillar[5]arene has 8 possible conformers: 4 diastereomers and 2 enantiomers (Fig. 9) resulting from planar chirality. Solid state pillar[5]arenes exist in racemic forms, an example of which is permethylated pillar[5]arene (**1**) where planar-chiral (*pS*)- and (*pR*)-**1** forms co-exist in a 1:1 proportion (Fig. 10). Planar-chiral compounds are structurally interesting and have potential as frameworks for functional materials such as chiral discriminators [80, 81], chiral polymers and supramolecules [82, 83], as well as guest receptors [84]. The rotation of the units leads to the exchange of conformers and racemization, so inhibiting the rotational motion is necessary for isolating planar-chiral pillar[5]arenes. We have investigated the rotational motion of pillar[5]arene units with the objective of a isolating planar-chiral pillar[5]arene, and dynamic ^{1}H NMR was used to probe the rotational behavior.

Perhydroxylated pillar[5]arene

In perhydroxylated pillar[5]arene **6**, ^{1}H NMR peaks from phenol, benzene and methylene bridge moieties appeared as singlets at 30 °C (Fig. 11a). However, complex split peaks were observed at −90 °C due to decreased rotational movement on the NMR time scale. The flipping of the units occurs due to the *intra*-molecular hydrogen bond belt [85], which is observed in the crystalline state of **6** (Fig. 2d).

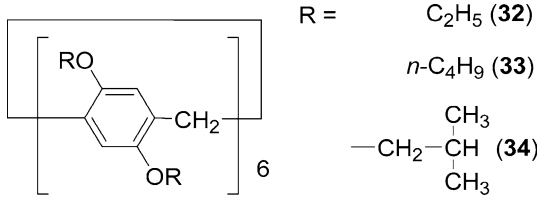


Fig. 8 Chemical structures of pillar[6]arenes

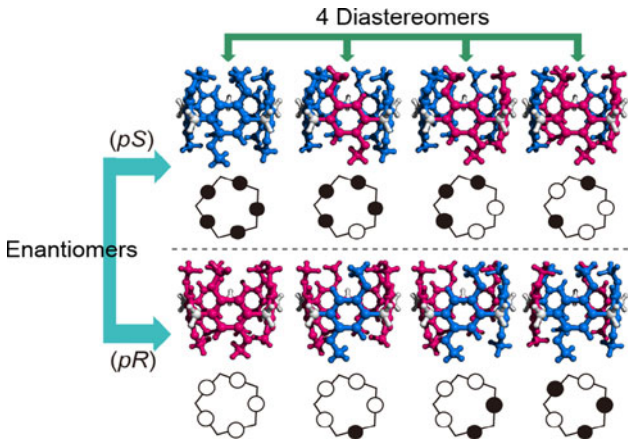


Fig. 9 Conformers of pillar[5]arene

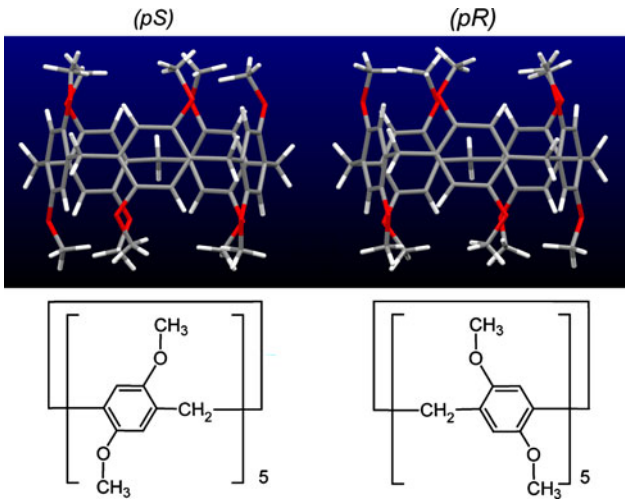


Fig. 10 Enantiomers of permethylated pillar[5]arene (**1**) in X-ray crystalline analysis

Permethylated pillar[5]arene

Dynamic ^{1}H NMR was employed to examine the rotational behavior of permethylated pillar[5]arene (**1**), however, ^{1}H NMR peaks of **1** showed no splitting at −90 °C (Fig. 11b). The rotation of phenolic units remained fast at −90 °C due to the lack of the *inter*-molecular hydrogen bond belt [85].

Peralkylated pillar[5]arenes

We synthesized pillar[5]arenes containing alkyl chains at both rims (**19**–**24**) for the purpose of isolating planar-chiral pillar[5]arene. The ^{1}H NMR signals from the methylene moieties adjacent to the O atoms (peak c) split into two groups of peaks in a 1:1 ratio at a low temperature (Fig. 11c). The positions of the two methylene protons are magnetically non-equivalent due to the planar chirality of

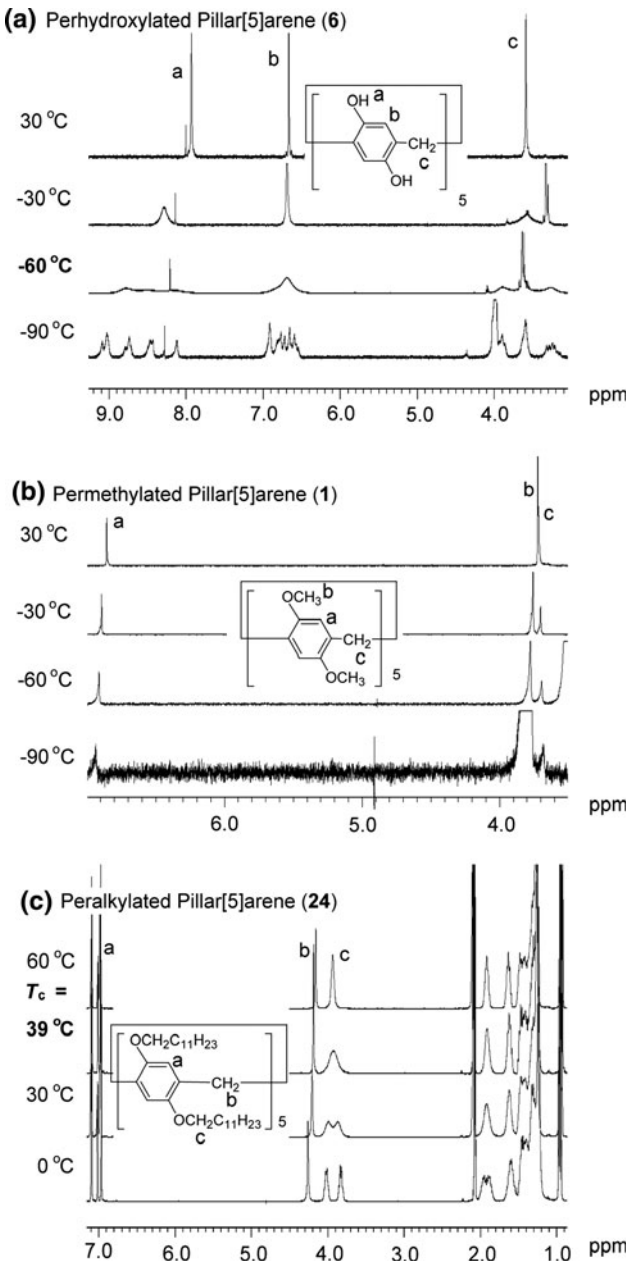


Fig. 11 Variable temperature ^{1}H NMR spectra of **a** perhydroxylated pillar[5]arene (**6**) in acetone-d_6, **b** permethylated pillar[5]arene (**1**) in acetone-d_6 and perdodecylated pillar[5]arene (**24**) in toluene-d_8. Reprinted with permission from Refs. [67] and [85]

pillar[5]arene. However, at a high temperature the magnetically non-equivalent positions can be *inter*-changeable via ring flipping. Thus, splitting of the proton resonances are a useful probe for determining the rotational barrier of the units on the NMR timescale, and coalescence temperatures are summarized in Table 1. Introducing long dodecyl chains at both rims (**24**) resulted in coalescence of the proton signals of the methylene moieties adjacent to O atoms, and indicated that rotation took place [66].

Introducing long alkyl chains cannot inhibit rotational motion, so we synthesized pillar[5]arenes with bulkier cyclohexyl substituents at both rims including per-cyclohexylmethyl-(**9**) and percyclohexylethylpillar[5]arenes (**10**). Heating caused the methylene peaks of **10** to begin to merge, indicating that rotation occurred on the NMR timescale at an elevated temperature. In contrast, methylene proton resonances in **9** barely changed with heating, indicating that rotation either did not take place or was extremely slow. Chiral HPLC measurements were carried out to further investigate the rotational motion of **9**. Injecting **9** onto an appropriate chiral HPLC column gave two peaks of equal area, and fractions were isolated with the first fraction then re-injected. The original first peak was found but the second peak from the paired enantiomer was not observed. Even after holding at 40 °C for 18 h, the second peak was not observed. Similar trends were also observed for the re-injection of the second fraction, indicating that enantiomers of **9** do not racemize. Figure 12a and b show UV–Vis and circular dichroism (CD) spectra of each fraction. The CD spectra of the fractions appear as mirror images, indicating the isolation of enantiopure (*pS*)- and (*pR*)-**9**. Introducing cyclohexylmethyl arms onto the pillar[5]arene rims inhibited the rotational motion and enabled the isolation of (*pS*)- and (*pR*)-**9** enantiomers from racemic mixtures [56].

The introduction of chiral substituents at both rims afforded planar-chiral pillar[5]arene (**26**). Compound **26** exhibited planar chirality and interconversion between (*pS*)-**26** and (*pR*)-**26** occurred. The diastereomeric excess of **26** was relatively small, so the introduction of bulky chiral substituents and/or many asymmetric carbon moieties at the rims enhances diastereomeric excess [69].

Host–guest properties of pillar[5]arenes

The internal cavity size of permethylated pillar[5]arene (**1**) as determined from single X-ray analysis is approximately 5 Å, which is analogous to that for cucurbit[6]uril and α-CD [50]. The cavity size of these three species can accommodate an alkyl chain or a benzene ring. Association constants and stoichiometry between pillar[5]arene derivatives and guest molecules are summarized in Table 1 and Fig. 13. Complexation of peralkylated pillar[5]arenes forms complexes with cationic guest molecules in $CDCl_3$ (runs 15, 17–20). Complexation of perhydroxylated pillar[5]arene **6** with electron accepting guests were observed in polar solvents and the complexation property largely depended on the polarity of the solvents (runs 1–14). Formation of complexes between the cationic guests and water-soluble pillar[5]arene (run 16) were also described.

Peralkylated pillar[5]arenes

Peralkylated pillar[5]arenes form 1:1 complexes with *n*-octatrimethyl ammonium hexafluorophosphate (**OTMA**, Fig. 13) in $CDCl_3$. The complexation of **OTMA** with **26** and **29** was a rapid exchange on the NMR time scale at 25 °C, while complexation of **OTMA** with **9**, **28** and **30** was very slow under the same conditions.

Perhydroxylated pillar[5]arenes

Electrostatic effects play an important role in molecular recognition in aqueous and organic solutions. In cucurbit[7]uril, portals carry a significant negative charge. Thus cucurbit[7]uril favors binding of cationic guests [37]. Figure 14 shows the calculated electrostatic potential profiles of perhydroxylated pillar[5]arene (**6**). These DFT calculations were carried out using a B3LYP/6-311G(d,p) level of theory. Like cucurbit[7]uril, the electrostatic potential of the cavity of **6** was significantly negative, and thus the binding of guests with a positive charge was favored. Our group reported the host–guest properties of **6**, and the formation of a 1:1 host–guest complex took place when octylviologen salt (**C8DBpy**, Fig. 13) was employed as the guest [44]. Complexation was confirmed by NMR, UV–Vis and fluorescence measurements. ^{1}H NMR signals from viologen and the methylene moieties adjacent to N atoms shifted upfield, whereas the other proton resonances showed little change. NOE correlations in the 2D NOESY analysis were observed between the phenyl protons of **6** and viologen moieties of **C8DBpy**. These observations indicate that the viologen group of **C8DBpy** was included in the cavity of **6**. The constituent unit hydroquinone showed an emission at 333 nm on excitation at 279 nm, and thus **6** also exhibited the same emission. When the electron accepting guest **C8DBpy** was added to **6**, the fluorescence was quenched, due to the formation of a charge-transfer complex between **6** and **C8DBpy**. This was confirmed by UV–Vis measurements, and their mixing caused the solution color to change from colorless to yellow. The absorption spectrum of 1:1 mixtures of **6** and **C8DBpy** differed from the sum of the spectra of the individual species. A broad absorption band at around 700 nm was ascribed to the charge-transfer complex between **C8DBpy** and pillar[5]arene. The association constants between **6** and **C8DBpy** were able to be calculated from spectroscopic data (Table 2). The association constant of the complex in DMSO-d_6 is weaker than in acetone-d_6, methanol-d_3 and acetonitrile-d_3 (runs 8–11). [86]. During the course of complexation of **6** with these positively charged guests, cation–π interactions should be the important driving forces, which are dramatically affected by solvent polarity. The formation of host–guest

Table 1 Coalescence temperatures for pillar[5]arenes

Pillar[5]arenes	Solvent	MHz	Coalescence Temperature	Ref.
1[a]	Toluene-d_8	400	No split at −90 °C	[85]
6[b]	Acetone-d_6	400	ca. −60 °C	[85]
9[c]	Toluene-d_8	500	Split at 90 °C	[56]
10[c]	Toluene-d_8	500	Coalescing at 90 °C	[56]
11[c]	DMF-d_7	400	No split at −50 °C	[57]
12[c]	DMF-d_7	400	46 °C	[57]
13[c]	D_2O	400	No split at 25 °C	[57]
19[c]	Toluene-d_8	400	−41 °C	[67]
20[c]	Toluene-d_8	400	−21 °C	[67]
21[c]	Toluene-d_8	400	−14 °C	[67]
22[c]	Toluene-d_8	400	−4 °C	[67]
23[c]	Toluene-d_8	400	1 °C	[67]
24[c]	Toluene-d_8	400	39 °C	[67]
25[c]	Toluene-d_8	500	75 °C	[68]
28[c]	Toluene-d_8	500	ca. −40 °C	[72]
29[c]	Toluene-d_8	500	−45 °C	[73]
30[c]	Toluene-d_8	500	−15 °C	[73]

[a] The proton signals from the methoxy, methylene bridge and benzene were measured

[b] The proton signals from the OH methylene bridge and benzene were measured

[c] The proton signals from the methylene moieties adjacent to O atoms were measured

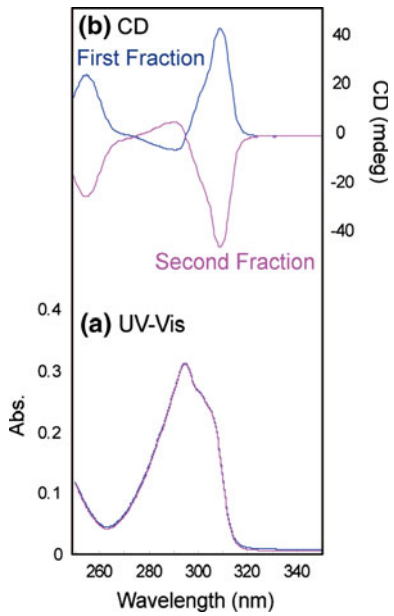


Fig. 12 **a** UV–Vis and **b** CD spectra of the first and second fractions of **9** (14 μL $mol^{-1}cm^{-1}$) in hexane at 25 °C. Reprinted permission from Ref. [56]

complexes of ionic liquids (ILs) with pillar[5]arene has also been reported. ILs are cationic electron accepting molecules similar to viologen derivatives, and we have investigated host–guest complexes between pillar[5]arene and ILs in organic media (runs 13, 14). Compound **6** formed 1:2 host–guest complexes with ILs, which were the first reported examples of a 1:2 pillar[5]arene-guest complexes [87].

Percarboxylated pillar[5]arenes

Pillar[5]arenes exhibit interesting host–guest properties in organic media, in sharp contrast to CDs and cucurbit[*n*]urils which form host–guest complexes more readily in aqueous media. This difference results from the driving force for the complexation. In CDs and cucurbit[*n*]urils, the main driving force is hydrophobic-hydrophilic interactions in aqueous media. The hydrophobic-hydrophilic interaction is only operative in aqueous media. Accordingly, we synthesized water-soluble percarboxylated pillar[5]arene (**13**) by modification of rim OH groups of perhydroxylated pillar[5]arene (**6**). Compound **13** contains electron donor dialkoxybenzene moieties and has carboxylate anions at both rims, and thus the cationic electron accepting dimethyl viologen salt (**C1DBpy**, Fig. 13) was used as the guest. **13** formed a very stable 1:1 complex with **DMeBpy** in aqueous media ($K_1 = 8.2 \pm 1.7 \times 10^4\ M^{-1}$) [57]. Electrostatic, charge-transfer and hydrophobic-hydrophilic interactions stabilized this host–guest complexation. The combinations of water-soluble pillar[5]arene **13** with hetero-macrocyclic water-soluble receptors such as CDs and cucurbiturils will open new directions in supramolecular chemistry, since multiple interactions between two or more complex molecules give insights into the molecular recognition and self-assembly processes.

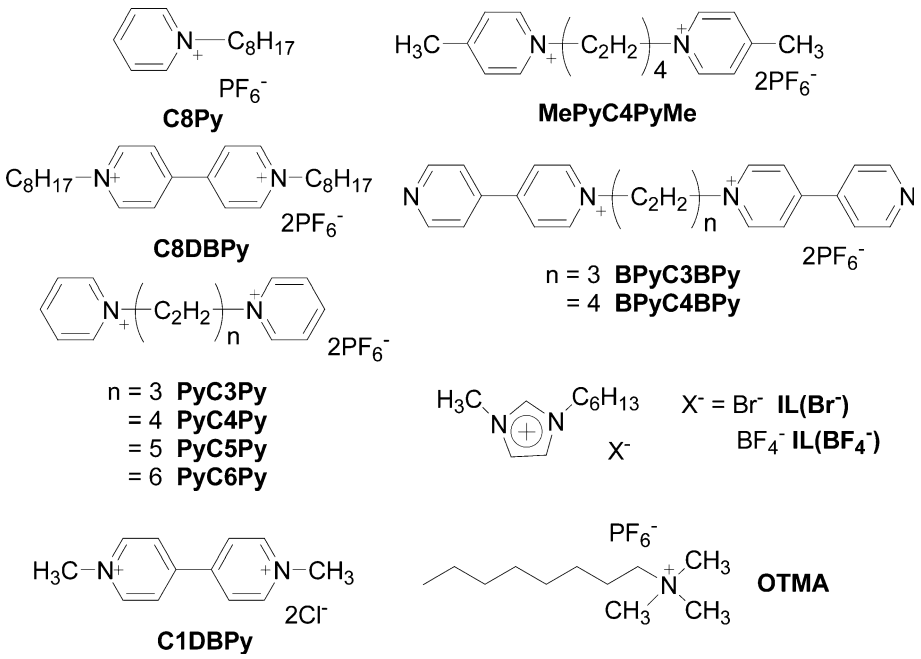


Fig. 13 Chemical structures of guest molecules for pillar[5]arenes

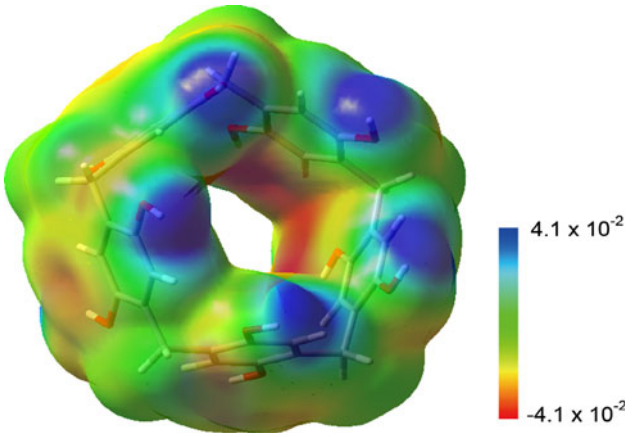


Fig. 14 Electrostatic potential profiles of pillar[5]arene

Supramolecular architectures constructed from pillar[5]arenes

Pillar[5]arenes form complexes with electron accepting guests. The pillar-shape and π-electron rich cavity make these hosts suitable for developing supramolecular architectures such as rotaxanes, catenanes, polyrotaxanes and polycatenanes. They also have potential application in the construction of nano-materials. There exists the possibility of using pillar[5]arene as a new building block instead of classical hosts, leading to the creation of new functional and structural supramolecular materials.

Pillar[5]arene-based *pseudo*rotaxanes and rotaxanes

Perhydroxylated pillar[5]arene (**6**) forms host–guest complexes with electron accepting viologen, pyridinium and imidazolium cations. The molecular design of these cationic molecules is very simple, and reliable procedures for their synthesis are well-established [88]. These cationic molecules have therefore been exploited in the construction of pillar[5]arene-based supramolecules. The dication, 1,4-bis[*N*-(*N*′-hydroimidazolium)]butane, can be threaded through the cavity of **6** to construct a stable [2]*pseudo*rotaxane, and the dethreading/rethreading process can be reversibly controlled by acid–base stimulus [89]. The formation of an ion-pair stoppered [2]*pseudo*rotaxane [58] and [2]rotaxane [90] was also recently reported by Hou and Stoddart groups, respectively.

Poly*pseudo*rotaxanes and polyrotaxanes constructed from perhydroxylated pillar[5]arenes

Polyrotaxanes contain many cyclic molecules mechanically incorporated onto a polymer chain, and have attracted significant attention as new polymeric materials. CDs and crown ethers were initially utilized by Harada et al. as the macrocyclic components for polyrotaxanes. Poly*pseudo*rotaxanes where many α-CDs are threaded onto a polymer chain have been prepared from poly(ethylene glycol) and α-CDs [91]. CD-based polyrotaxanes have been prepared by capping the chain ends of the poly*pseudo*rotaxanes with bulky stoppers [92, 93]. Since these polyrotaxanes have many reactive OH groups from the CD moieties, they have been applied as topological gels and multivalent scaffolds [94–96]. Cucurbit[*n*]urils can also form very stable host–guest complexes with positively charged molecules in aqueous media, with poly*pseudo*rotaxanes and polyrotaxanes having previously been prepared from these species

Table 2 Association constants of pillar[5]arenes with guests

Run	Host	Guest	Solvent	Host:guest	Association constant (K) (M^{-1})	Method	Ref.
1	**6**	**C8Py**	Methanol	1:1	$1.2 \pm 0.3 \times 10^3$	fl	[44]
2	**6**	**C8DBpy**	Methanol	1:1	$1.2 \pm 0.2 \times 10^4$	fl	[44]
3	**6**	**PyC3Py**	DMSO	1:1	$8.8 \pm 0.7 \times 10$	uv	[86]
4	**6**	**PyC4Py**	DMSO	1:1	$4.5 \pm 0.4 \times 10^2$	uv	[86]
5	**6**	**PyC5Py**	DMSO	1:1	$3.7 \pm 0.3 \times 10^2$	uv	[86]
6	**6**	**PyC6Py**	DMSO	1:1	$1.2 \pm 0.1 \times 10^2$	uv	[86]
7	**6**	**MePyC4PyMe**	DMSO-d_6	1:1	$4.0 \pm 0.3 \times 10^2$	nmr	[86]
8	**6**	**BpyC4Bpy**	DMSO-d_6	1:1	$7.4 \pm 0.3 \times 10^2$	nmr	[86]
9	**6**	**BpyC4Bpy**	DMSO-d_6:CD_3OD	1:1	$2.3 \pm 0.2 \times 10^3$	nmr	[86]
10	**6**	**BpyC4Bpy**	DMSO-d_6:CD_3CN	1:1	$4.9 \pm 0.1 \times 10^3$	nmr	[86]
11	**6**	**BpyC4Bpy**	DMSO-d_6:$(CD_3)_2CO$	1:1	$5.4 \pm 0.2 \times 10^3$	nmr	[86]
12	**6**	**BpyC3Bpy**	DMSO-d_6	1:1	$1.2 \pm 0.2 \times 10^2$	nmr	[86]
13	**6**	**IL(Br^-)**	Acetone-d_6	1:2	$K_1 = 1.1 \times 10^2$ $K_2 = 2.0 \times 10$	nmr	[87]
14	**6**	**IL(BF_4^-)**	Acetone-d_6	1:2	$K_1 = 7.0 \times 10^2$ $K_2 = 1.7$	nmr	[87]
15	**9**	**OTMA**	$CDCl_3$	1:1	8.3×10^2	nmr	[56]
16	**13**	**C1DBpy**	H_2O	1:1	$8.2 \pm 1.7 \times 10^4$	fl	[57]
17	**26**	**OTMA**	$CDCl_3$	1:1	1.3×10^3	nmr	[69]
18	**28**	**OTMA**	$CDCl_3$	1:1	$6.3 \pm 0.3 \times 10^3$	nmr	[72]
19	**29**	**OTMA**	$CDCl_3$	1:1	$3.0 \pm 0.1 \times 10^3$	nmr	[73]
20	**30**	**OTMA**	$CDCl_3$	1:1	$4.1 \pm 0.4 \times 10^3$	nmr	[73]

[97–101]. Following the host–guest complexation between perhydroxylated pillar[5]arene (**6**) and viologen derivatives, we synthesized a poly*pseudo*rotaxane constructed from **6** as the cyclic components and viologen polymer as the polymeric chain (Fig. 15). Mixing **6** and the viologen polymer led to the formation of a poly*pseudo*rotaxane. In contrast, mixing **6** with the viologen polymer with adamantyl groups at both ends did not give a poly*pseudo*rotaxane because of the bulkiness of the adamantyl stopper. This observation implies that **6** was threaded onto the viologen polymer axis from its both ends [102].

The adamantyl group is a suitable stopper for synthesis of the polyrotaxane from **6** and viologen polymer. We prepared a polyrotaxane by a facile one-pot synthesis, involving the mixing viologen polymer and **6**, which quickly led to complexation. Excess 1-adamantyl bromomethyl ketone was then added, and the reaction was heated at 100 °C for 6 h, during which time precipitates formed. The reaction mixture was evaporated to dryness and the residue was washed several times with acetonitrile to give the polyrotaxane. The pillar[5]arene-based polyrotaxane was isolated in an extremely high yield (93%), due to the high stability of the complexes between **6** and the viologen polymer [103]. Such stability in organic media is quite different from that of CD-based poly*pseudo*rotaxanes [104]. Compound **6** and the viologen polymer are soluble in various solvents such as acetone, acetonitrile, methanol, DMF and DMSO, while polyrotaxane is soluble in DMF and DMSO and but insoluble in the other organic solvents. The formation of *inter*-molecular hydrogen bonds between the OH moieties of **6** not only stabilized the structure but also reduced solubility.

Huang and coworker reported that a linear supramolecular polymer has been constructed using copillar[5]arene (**31**) as a monomer. An octyl group on the pillar[5]arene rim was included in the cavity of another copillar[5]arene. A continuous inclusion of the octyl groups afforded a pillar[5]arene-based linear supramolecular polymer [74].

Conclusion and outlook

This review covers macrocyclic host pillar[5]arene derivatives with reference to their synthesis, rotational properties, host–guest chemistry and application as supramolecular materials. Chemical structures of pillar[5]arenes are generally quite simple, show interesting functionality and host–guest properties. They can be used as building blocks for the construction of supramolecular architectures. Differences in the position of methylene bridges result in their characteristic pillar-architecture and planar chirality, in comparison to

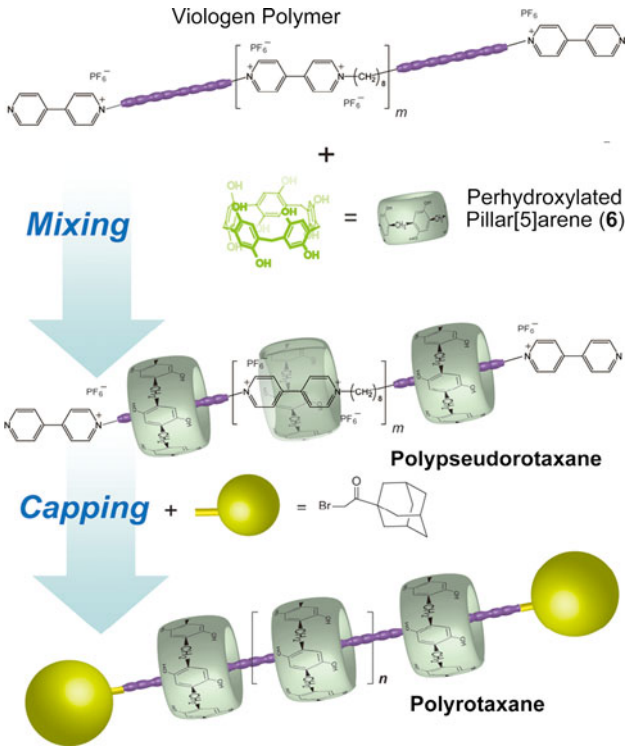


Fig. 15 Synthesis of polyrotaxane from **6**

those of calix[*n*]arenes. Perhydroxylated pillar[5]arene (**6**) has 10 reactive OH groups similar to CDs, and their modification has been studied to introduce further functionality. Compound **6** is regarded as an organic-soluble CD. Pillar[5]arenes form inclusion complexes with electron accepting guests, and the host–guest properties of pillar[5]arene are analogous to those of cucurbit[*n*]urils. Since the first our report in 2008 [44], there are now around thirty pillar[5]arene derivatives which have been reported in around twenty articles from numerous groups. Pillararene chemistry is expected to make rapid advances in the coming years.

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References

1. Nepogodiev, S.A., Stoddart, J.F.: Cyclodextrin-based catenanes and rotaxanes. Chem. Rev. **98**, 1959–1976 (1998). doi:10.1021/cr970049w
2. Sauvage, J.P.: Transition metal-containing rotaxanes and catenanes in motion: toward molecular machines and motors. Acc. Chem. Res. **31**, 611–619 (1998). doi:10.1021/10.1021/ar960263r
3. Fujita, M.: Self-assembly of [2]catenanes containing metals in their backbones. Acc. Chem. Res. **32**, 53–61 (1999). doi:10.1021/ar9701068
4. Wenz, G., Han, B.H., Müller, A.: Cyclodextrin rotaxanes and polyrotaxanes. Chem. Rev. **106**, 782–817 (2006). doi:10.1021/cr970027+
5. Harada, A.: Cyclodextrin-based molecular machines. Acc. Chem. Res. **34**, 456–464 (2001). doi:10.1021/ar000174l
6. Stoddart, J.F.: Molecular machines. Acc. Chem. Res. **34**, 410–411 (2001). doi:10.1021/ar010084w
7. Collin, J.P., Buchecker, C.D., Gaviña, P., Molero, M.C.J., Sauvage, J.P.: Shuttles and muscles: linear molecular machines based on transition metals. Acc. Chem. Res. **34**, 477–487 (2001). doi:10.1021/ar0001766
8. Niu, Z., Gibson, H.W.: Polycatenanes. Chem. Rev. **109**, 6024–6046 (2009). doi:10.1021/cr900002h
9. Cantrill, S.J., Chichak, K.S., Peters, A.J., Stoddart, J.F.: Nanoscale borromean rings. Acc. Chem. Res. **38**, 1–9 (2005). doi:10.1021/ar040226x
10. Harada, A., Hashidzume, M., Yamaguchi, H., Takashima, Y.: Polymeric rotaxanes. Chem. Rev. **106**, 782–817 (2009). doi:10.1021/cr970027+
11. Okumura, Y., Ito, K.: The polyrotaxane gel: a topological gel by figure-of-eight cross-links. Adv. Mater. **13**, 485–487 (2001). doi:10.1002/1521-4095(200104)13:7<485:AID-ADMA485>3.0.CO;2-T
12. Araki, J., Ito, K.: Recent advances in the preparation of cyclodextrin-based polyrotaxanes and their applications to soft materials. Soft Matter. **3**, 1456–1473 (2007). doi:10.1039/B705688E
13. Thoma, J.A., Stewart, M.L. (eds.): Starch: Chemistry and Technology. Academic Press, New York (1965)
14. Bender, M.L., Komiyama, M. (eds.): Bioorganic Chemistry. Academic Press, New York (1977)
15. Harata, K.: Structural aspects of stereodifferentiation in the solid state. Chem. Rev. **98**, 1803–1827 (1998). doi:10.1021/cr9700134
16. Pedersen, C.J.: Cyclic polyethers and their complexes with metal salts. J. Am. Chem. Soc. **89**, 7017–7036 (1967). doi:10.1021/ja01002a035
17. Dye, J.L.: Electrides: early examples of quantum confinement. Acc. Chem. Res. **42**, 1564–1572 (2009). doi:10.1021/ar9000857
18. Mezei, G., Zaleski, C.M., Pecoraro, V.L.: Structural and functional evolution of metallacrowns. Chem. Rev. **107**, 4933–5003 (2007). doi:10.1021/cr078200h
19. Gutsche, C.D. (ed.): Calixarenes. The Royal Society of Chemistry, Cambridge (1989)
20. Vicens, J., Böhmer, V. (eds.): Calixarenes: A Versatile Class of Macrocyclic Compounds. Kluwer Academic, Dordrecht, the Netherlands (1991)
21. Ikeda, A., Shinkai, S.: Novel cavity design using calix[*n*]arene skeletons: toward molecular recognition and metal binding. Chem. Rev. **97**, 1713–1734 (1997). doi:10.1021/cr960385x
22. Casnati, A., Sansone, F., Ungaro, R.: Peptido- and glycocalixarenes: playing with hydrogen bonds around hydrophobic cavities. Acc. Chem. Res. **36**, 246–254 (2003). doi:10.1021/ar0200798
23. Tahara, K., Yobe, Y.: Molecular loops and belts. Chem. Rev. **106**, 5274–5290 (2006). doi:10.1021/cr050556a
24. Kaleta, J., Mazal, C.: A triangular macrocycle altering planar and bulky sections in its molecular backbone. Org. Lett. **13**, 1326–1329 (2011). doi:10.1021/ol1031816
25. Gessner, V.H., Tilley, T.D.: Diphenylanthracene macrocylces from reductive zirconocene coupling: on the edge of steric

overload. Org. Lett. **13**, 1154–1157 (2011). doi:10.1021/ol2000099
26. Chen, G., Mahmud, I., Dawe, L.N., Daniels, L.M., Zhao, Y.: Synthesis and properties of conjugated oligoyne-centered π-extended tetrathiafulvalene analogues and related macromolecular systems. J. Org. Chem. **76**, 2701–2715 (2011). doi:10.1021/jo2000447
27. Tominaga, M., Masu, H., Azumaya, I.: Construction and charge-transfer complexation of adamantane-based macrocycles and a cage with aromatic ring moieties. J. Org. Chem. **74**, 8754–8760 (2009). doi:10.1021/jo9018842
28. Tominaga, M., Masu, H., Katagiri, K., Kato, T., Azumaya, I.: Triple helicate constructed by covalent bondings: crystal structure and effective synthesis based on propeller-like substructures. Org. Lett. **7**, 3785–3787 (2005). doi:10.1021/ol051477o
29. Lou, K., Prior, A.M., Desper, J., Hua, D.H.: Synthesis of cyclododeciptycene quinones. J. Am. Chem. Soc. **132**, 17635–17641 (2010). doi:10.1021/ja1088309
30. Shorthill, B.J., Avetta, C.T., Glass, T.E.: Shape-selective sensing of lipids in aqueous solution by a designed fluorescent molecular tube. J. Am. Chem. Soc. **126**, 12732–12733 (2004). doi:10.1021/ja047639d
31. Yokoyama, A., Maruyama, T., Tagami, K., Masu, H., Katagiri, K., Azumaya, I., Yokozawa, T.: One-pot synthesis of cyclic triamides with a triangular cavity from trans-stilbene and diphenylacetylene monomers. Org. Lett. **10**, 3207–3210 (2008). doi:10.1021/ol801083r
32. Sarri, P., Venturi, F., Cuda, F., Roelens, S.: Binding of acetylcholine and tetramethylammonium to flexible cyclophane receptors: improving on binding ability by optimizing host's geometry. J. Org. Chem. **69**, 3654–3661 (2004). doi:10.1021/jo049899j
33. Rossom, W.V., Robeyns, K., Ovaere, M., Meervelt, L.V., Dehaen, W., Maes, W.: Odd-numbered oxacalix[*n*]arenes ($n = 5$, 7): synthesis and solid-state structures. Org. Lett. **13**, 126–129 (2011). doi:10.1021/ol1026969
34. Freeman, W.A., Mock, W.L., Shih, N.Y.: Cucurbituril. J. Am. Chem. Soc. **103**, 7367–7368 (1981). doi:10.1021/ja00414a070
35. Kim, J., Jung, I.S., Kim, S.Y., Lee, E., Kang, J.K., Sakamoto, S., Yamaguchi, K., Kim, K.: New cucurbituril homologues: syntheses, isolation, characterization, and X-ray crystal structures of cucurbit[*n*]uril ($n = 5$, 7, and 8). J. Am. Chem. Soc. **122**, 540–541 (2000). doi:10.1021/ja993376p
36. Lee, J.W., Samal, S., Selvapalam, N., Kim, H.J., Kim, K.: Cucurbituril homologues and derivatives: new opportunities in supramolecular chemistry. Acc. Chem. Res. **36**, 621–630 (2000). doi:10.1021/ar020254k
37. Lagona, J., Mukhopadhyay, P., Chakrabarti, S., Isaacs, L.: The cucurbituril family. Angew. Chem. Int. Ed. **44**, 4844–4870 (2005). doi:10.1002/anie.200460675
38. Svec, J., Necas, M., Sindelar, V.: Bambus[6]uril. Angew. Chem. Int. Ed. **49**, 2378–2381 (2010). doi:10.1002/anie.201000420
39. Day, A., Arnold, A.P., Blanch, R.J., Shushall, B.: Controlling factors in the synthesis of cucurbituril and its homologues. J. Org. Chem. **66**, 8094–8100 (2001). doi:10.1021/jo015897c
40. Furukawa, S., Uji-i, H., Tahara, K., Ichikawa, T., Sonoda, M., De Schryver, F.C., Tobe, Y., De Feyter, S.: Molecular geometry directed kagomé and honeycomb networks: toward two-dimensional crystal engineering. J. Am. Chem. Soc. **128**, 3502–3503 (2006). doi:10.1021/ja0583362
41. Miyake, K., Yasuda, S., Harada, A., Sumaoka, J., Komiyama, M., Shigekawa, H.: Formation process of cyclodextrin necklace—analysis of hydrogen bonding on a molecular level. J. Am. Chem. Soc. **125**, 5080–5085 (2003). doi:10.1021/ja026224u
42. Shigekawa, H., Miyake, K., Sumaoka, J., Harada, A., Komiyama, M.: The molecular abacus: STM manipulation of cyclodextrin necklace. J. Am. Chem. Soc. **122**, 5411–5412 (2000). doi:10.1021/ja000037j
43. Nishimura, D., Takashima, Y., Aoki, H., Takahashi, T., Yamaguchi, H., Ito, S., Harada, A.: Single-molecular imaging of rotaxane based on glass substrates: observations of rotary movement of a rotor. Angew. Chem. Int. Ed. **47**, 6077–6079 (2008). doi:10.1002/anie.200801431
44. Ogoshi, T., Kanai, S., Fujunami, S., Yamagishi, T., Nakamoto, Y.: *Para*-bridged symmetrical pillar[5]arenes: their lewis acid-catalyzed synthesis and host-guest property. J. Am. Chem. Soc. **130**, 5022–5023 (2008). doi:10.10210.1021/ja711260m
45. Ogoshi, T., Aoki, T., Kitajima, K., Fujinami, S., Yamagishi, T., Nakamoto, Y.: Facile, rapid, and high-yield synthesis of pillar[5]arene from commercially available reagents and its X-ray crystal structure. J. Org. Chem. **76**, 328–331 (2011). doi:10.1021/jo1020823
46. Gribble, G.W., Nutaitis, C.F.: [1.1.1.1.1]Paracyclophane and [1.1.1.1.1.1]paracyclophane. Tetrahedron Lett. **26**, 6023–6026 (1985). doi:10.1016/S0040-4039(00)95115-3
47. Ogoshi, T., Kitajima, K., Umeda, K., Hiramitsu, S., Kanai, S., Fujinami, S., Yamagishi, T., Nakamoto, Y.: Lewis acid-catalyzed synthesis of dodecamethoxycalix[4]arene from 1,3,5-trimethoxybenzene and its conformational behavior and host–guest property. Tetrahedron **65**, 10644–10649 (2009). doi:10.1016/j.tet.2009.10.059
48. Mclldowie, M.J., Mocerino, M., Skelton, B.W., White, A.H.: Facile lewis acid catalyzed synthesis of *C4* symmetric resorcinarenes. Org. Lett. **2**, 3869–3871 (2000). doi:10.1021/ol006608u
49. Iwanek, W., Urbaniak, M., Bocheńska, M.: The template synthesis and complexation properties of methoxypyrogallo[4]arene. Tetrahedron **58**, 2239–2243 (2002). doi:10.1016/S0040-4020(02)00097-2
50. Rekharsky, M.V., Inoue, Y.: Complexation thermodynamics of cyclodextrins. Chem. Rev. **98**, 1875–1918 (1998). doi:10.1021/cr970015o
51. Negishi, E., Anastasia, L.: Palladium-catalyzed alkynylation. Chem. Rev. **103**, 1979–2018 (2003). doi:10.1021/cr020377i
52. Moore, J.S.: Shape-persistent molecular architectures of nanoscale dimension. Acc. Chem. Res. **30**, 402–413 (1997). doi:10.1021/ar950232g
53. Sonogashira, K., Tohda, Y., Hagiwara, N.: A convenient synthesis of acetylenes: catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes and bromopyridines. Tetrahedron Lett. **16**, 4467–4470 (1975). doi:10.1016/S0040-4039(00)91094-3
54. Chen, Q.Y., Yang, Z.Y.: Palladium-catalyzed reaction of phenyl fluoroalkanesulfonates with alkynes and alkenes. Tetrahedron Lett. **27**, 1171–1174 (1986). doi:10.1016/S0040-4039(00)84208-2
55. Ogoshi, T., Umeda, K., Yamagishi, T., Nakamoto, Y.: Through-space π-delocalized pillar[5]arene. Chem. Commun. 4874–4876 (2009). doi:10.1039/b907894k
56. Ogoshi, T., Masaki, K., Shiga, R., Kitajima, K., Yamagishi, T.: Planar-chiral macrocyclic host pillar[5]arene: no rotation of units and isolation of enantiomers by introducing bulky substituents. Org. Lett. **13**, 1264–1266 (2011). doi:10.1021/ol200062j
57. Ogoshi, T., Hashizume, M., Yamagishi, T., Nakamoto, Y.: Synthesis, conformational and host–guest properties of water-soluble pillar[5]arene. Chem. Commun. **46**, 3708–3710 (2010). doi:10.1039/c0cc00348d
58. Hu, X.B., Chen, L., Si, W., Yu, Y., Hou, J.L.: Pillar[5]arene decaamine: synthesis, encapsulation of very long linear diacids and formation of ion pair-stopped [2]rotaxanes. Chem. Commun. **47**, 4694–4696 (2011). doi:10.1039/c1cc10633c

59. Ogoshi, T., Shiga, R., Hashizume, M., Yamagishi, T.: "Clickable" pillar[5]arenes. Chem. Commun. **47**, 6927–6929 (2011). doi:10.1039/c1cc11864a
60. Takahashi, K., Hattori, K., Toda, F.: Monotosylated α- and β-cyclodextrins prepared in an alkaline aqueous solution. Tetrahedron Lett. **25**, 3331–3334 (1984). doi:10.1016/S0040-4039(01)81377-0
61. Ikeda, H., Nagano, Y., Du, Y.-q., Ikeda, T., Toda, F.: Modifications of the secondary hydroxyl side of α-cyclodextrin and NMR studies of them. Tetrahdron Lett. **31**, 5045–5048 (1990). doi:10.1016/S0040-4039(00)97802-X
62. Villalonga, R., Cao, R., Fragoso, A.: Supramolecular chemistry of cyclodextrins in enzyme technology. Chem. Rev. **107**, 3088–3116 (2007). doi:10.1021/cr050253g
63. Pearce, A.J., Sinaÿ, P.: Diisobutylaluminum-promoted regioselective *de-O*-benzylation of perbenzylated cyclodextrins: a powerful new strategy for the preparation of selectively modified cyclodextrins. Angew. Chem. Int. Ed. **39**, 3610–3612 (2000). doi:10.1002/1521-3773(20001016)39:20<3610:AID-ANIE3610>3.0.CO;2-V
64. Jon, S.Y., Selvapalam, N., Oh, D.H., Kang, J.K., Kim, S.Y., Jeon, Y.J., Lee, J.W., Kim, K.: Facile synthesis of cucurbit[n]uril derivatives via direct functionalization: expanding utilization of cucurbit[n]uril. J. Am. Chem. Soc. **125**, 10186–10187 (2003). doi:10.1021/ja036536c
65. Ogoshi, T., Demachi, K., Kitajima, K., Yamagishi, T.: Monofunctionalized pillar[5]arenes: synthesis and supramolecular structure. Chem. Commun **47**, 7164–7166 (2011). doi:10.1039/c1cc12333e
66. Ogoshi, T., Kitajima, K., Fujinami, S., Yamagishi, T. Synthesis and X-ray crystal structure of difunctionalized pillar[5]arene at A1/B2 positions by in situ cyclization and deprotection. Chem. Commun. **47** (2011). doi:10.1039/c1cc13546e
67. Ogoshi, T., Kitajima, K., Aoki, T., Fujinami, S., Yamagishi, T., Nakamoto, Y.: Synthesis and conformational characteristics of alkyl-substituted pillar[5]arenes. J. Org. Chem. **75**, 3268–3273 (2010). doi:10.1021/jo100273n
68. Han, C., Ma, F., Zibin, Z., Xia, B., Yu, Y., Huang, F.: DIB-Pillar[*n*]arenes ($n = 5, 6$): syntheses, X-ray crystal structures, and complexation with *n*-octyltriethyl ammonium hexafluorophosphate. Org. Lett. **12**, 4360–4363 (2010). doi:10.1021/ol1018344
69. Ogoshi, T., Shiga, R., Yamagishi, T., Nakamoto, Y.: Planar-chiral pillar[5]arene: chiral switches induced by multi-external stimulus of temperature, solvents, and addition of achiral guest molecule. J. Org. Chem. **76**, 618–622 (2011). doi:10.1021/jo1021508
70. Ogoshi, T., Kitajima, K., Yamagishi, T., Nakamoto, Y.: Synthesis and conformational characteristics of nonsymmetric pillar[5]arene. Org. Lett. **12**, 636–638 (2010). doi:10.1021/ol902877w
71. Kou, Y., Tao, H., Cao, D., Fu, Z., Schollmeyer, D., Meier, H.: Synthesis and conformational properties of nonsymmetric pillar[5]arenes and their acetonitrile inclusion compounds. Eur. J. Org. Chem. **48**, 9721–9723 (2010). doi:10.1002/ejoc.201000718
72. Zibin, Z., Luo, Y., Xia, B., Han, C., Yu, Y., Chen, X., Huang, F.: Four constitutional isomers of BMpillar[5]arene: synthesis, crystal structures and complexation with *n*-octyltrimethyl ammonium hexafluorophosphate. Chem. Commun. **47**, 2417–2419 (2011). doi:10.1039/c0cc03732j
73. Zhang, Z., Xia, B., Han, C., Yu, Y., Huang, F.: Syntheses of copillar[5]arenes by co-oligomerization of different monomers. Org. Lett. **12**, 3285–3287 (2010). doi:10.1021/ol100883k
74. Zibin, Z., Luo, Y., Chen, J., Dong, S., Yu, Y., Ma, Z., Huang, F.: Formation of linear supramolecular polymers that is driven by C–H π interactions in solution and in the solid state. Angew. Chem. Int. Ed. **50**, 1397–1401 (2011). doi:10.1002/anie.201006693
75. Stewart, D.R., Gutsche, C.D.: Isolation, characterization, and conformational characteristics of *p*-tert-butylcalix[9–20]arenes. J. Am. Chem. Soc. **121**, 4136–4146 (1999). doi:10.1021/ja983964n
76. Huang, W.H., Liu, S., Zavalij, P.Y., Isaacs, L.: Nor-seco-cucurbit[10]uril exhibits homotropic allosterism. J. Am. Chem. Soc. **128**, 14744–14745 (2006). doi:10.1021/ja064776x
77. Cao, D., Kou, Y., Liang, J., Chen, Z., Wang, L., Meier, H.: A facile and efficient preparation of pillararenes and a pillarquinone. Angew. Chem. Int. Ed. **48**, 9721–9723 (2009). doi:10.1002/anie.200904765
78. Gutsche, C.D., Bauer, L.J. Calixarenes. 5. Dynamic NMR characteristics of *p-tert*-butylcalix[4]-arene and *p-tert*-butylcalix[8]arene. Tetrahedron Lett. **22**, 4763–4766 (1981). doi:10.1016/S0040-4039(01)92337-8
79. Iwamoto, K., Araki, K., Shinkai, S.: Conformations and structures of *tetra-O*-alkyl-*p*-tert-butylcalix[4]arenes. How is the conformation of calix[4]arenes immobilized? J. Org. Chem. **56**, 4955–4962 (1991). doi:10.1021/jo00016a027
80. Oi, S., Miyano, S.: Design and synthesis of chiral stationary phase derived from *(S)*-[10]paracyclophane-13-carboxylic acid for the HPLC separation of enantiomers. Chem. Lett. **21**, 987–990 (1992)
81. Hattori, T., Harada, N., Oi, S., Abe, H., Miyano, S.: 1,12-Dioxa[12](1,4)naphthalenophane-14-carboxylic acid: practical synthesis, resolution and absolute configuration of the enantiomers. Tetrahedron Asymmetr. **6**, 1043–1046 (1995). doi:10.1016/0957-4166(95)00120-E
82. Fiesel, R., Huber, J., Scherf, U.: Synthesis of an optically active poly(*para*-phenylene) ladder polymer. Angew. Chem. Int. Ed. **35**, 2111–2113 (1996). doi:10.1002/anie.199621111
83. Fiesel, R., Huber, J., Apel, U., Enkelmann, V., Hentschke, R., Scherf, U., Cabrera, K.: Novel chiral poly(*para*-phenylene) derivatives containing cyclophane-type moieties. Macromol. Chem. Phys. **198**, 2623–2650 (1997). doi:10.1002/macp.1997.021980901
84. Katoono, R., Kawai, H., Hujiwara, K., Suzuki, T.: [10]Paracyclophanediamides and their octadehydro derivatives: novel exotopic receptors with hydrogen-bonding sites on the bridge. Tetrahedron Lett. **45**, 8455–8459 (2004). doi:10.1016/j.tetlet.2004.09.115
85. Ogoshi, T., Kitajima, K., Aoki, T., Yamagishi, T., Nakamoto, Y.: Effect of an intramolecular hydrogen bond belt and complexation with the guest on the rotation behavior of phenolic units in pillar[5]arenes. J. Phys. Chem. Lett. **1**, 817–821 (2010). doi:10.1021/jz900437r
86. Li, C., Xu, Q., Li, J., Yao, F., Jia, X.: Complex interactions of pillar[5]arene with paraquats and bis(pyridinium) derivatives. Org. Biomol. Chem. **8**, 1568–1576 (2010). doi:10.1039/b920146g
87. Ogoshi, T., Tanaka, S., Yamagishi, T., Nakamoto, Y.: Ionic liquid molecules (ILs) as novel guests for pillar[5]arene: 1:2 host-guest complexes between pillar[5]arene and ILs in organic media. Chem. Lett. **40**, 96–98 (2011). doi:10.1246/cl.2011.96
88. Monk, P.M.S. (ed.): The Viologens Physicochemical Properties, Synthesis and Applications of the Salts of 4,4′-Bipyridine. Wiley, New York (1998)
89. Li, C., Zhao, L., Li, J., Ding, X., Chen, S., Zhang, Q., Yu, Y., Jia, X.: Self-assembly of [2]pseudorotaxanes based on pillar[5]arene and bis(imidazolium) cations. Chem. Commun. **46**, 9016–9018 (2010). doi:10.1039/c0cc03575k
90. Strutt, N.L., Forgan, R.S., Spruell, J.M., Botros, Y.Y., Stoddart, J.F.: Monofunctionalized pillar[5]arene as a host for

alkanediamines. J. Am. Chem. Soc. **133**, 5668–5671 (2011). doi:10.1021/ja111418j
91. Harada, A., Kamachi, M.: Complex formation between poly(ethylene glycol) and α-cyclodextrin. Macromolecules **23**, 2821–2823 (1990). doi:10.1021/ma00212a039
92. Harada, A.: Design and construction of supramolecular architectures consisting of cyclodextrins and polymers. Adv. Polym. Sci. **133**, 141–191 (1997). doi:10.1007/3-540-68442-5_4
93. Harada, A., Li, J., Kamachi, M.: The molecular necklace: a rotaxane containing many threaded α-cyclodextrins. Nature **356**, 325–327 (1992). doi:10.1038/356325a0
94. Ito, K.: Novel cross-linking concept of polymer network: synthesis, structure, and properties of slide-ring gels with freely movable junctions. Polym. J. **39**, 489–499 (2007). doi:10.1295/polymj.PJ2006239
95. Wu, Y.L., Li, J.: Synthesis of supramolecular nanocapsules based on threading of multiple cyclodextrins over polymers on gold nanoparticles. Angew. Chem. Int. Ed. **48**, 3842–3845 (2009). doi:10.1002/anie.200805341
96. Ooya, T., Eguchi, M., Yui, N.: Supramolecular design for multivalent interaction: maltose mobility along polyrotaxane enhanced binding with concanavalin A. J. Am. Chem. Soc. **125**, 13016–13017 (2003). doi:10.1021/ja034583z
97. Reczek, J.J., Kennedy, A.A., Halbert, B.T., Urbach, A.R.: Multivalent recognition of peptides by modular self-assembled receptors. J. Am. Chem. Soc. **131**, 2408–2415 (2009). doi:10.1021/ja808936y
98. Tan, Y., Choi, S.W., Lee, J.W., Ko, Y.H., Kim, K.: Synthesis and characterization of novel side-chain pseudopolyrotaxanes containing cucurbituril. Macromolecules **35**, 7161–7165 (2002). doi:10.1021/ma020534f
99. Ooya, T., Inoue, D., Choi, H.S., Kobayashi, Y., Loethen, S., Thompson, D.H., Ko, Y.H., Kim, K., Yui, N.: pH-responsive movement of cucurbit[7]uril in a diblock polypseudorotaxane containing dimethyl α-cyclodextrin and cucurbit[7]uril. Org. Lett. **8**, 3159–3162 (2006). doi:10.1021/ol060697e
100. Liu, Y., Ke, C.F., Zhang, H.Y., Wu, W.J., Shi, J.: Reversible 2D pseudopolyrotaxanes based on cyclodextrins and cucurbit[6]uril. J. Org. Chem. **72**, 280–283 (2007). doi:10.1021/jo0617159
101. Ogoshi, T., Masuda, K., Yamagishi, T., Nakamoto, Y.: Side-chain polypseudorotaxanes with heteromacrocyclic receptors of cyclodextrins (CDs) and cucurbit[7]uril (CB7): their contrast lower critical solution temperature behavior with α-CD, γ-CD, and CB7. Macromolecules **42**, 8003–8005 (2009). doi:10.1021/ma901474b
102. Ogoshi, T., Nishida, Y., Yamagishi, T., Nakamoto, Y.: Polypseudorotaxane constructed from pillar[5]arene and viologen polymer. Macromolecules **43**, 3145–3147 (2010). doi:10.1021/ma100079g
103. Ogoshi, T., Nishida, Y., Yamagishi, T., Nakamoto, Y.: High yield synthesis of polyrotaxane constructed from pillar[5]arene and viologen polymer and stabilization of its radical cation. Macromolecules **43**, 7068–7072 (2010). doi:10.1021/ma101320z
104. Zhao, T., Beckham, H.W.: Direct synthesis of cyclodextrin-rotaxanated poly(ethylene glycol)s and their self-diffusion behavior in dilute solution. Macromolecules **36**, 9859–9865 (2003). doi:10.1021/ma035513f