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Pillar[*n*]arene–calix[*m*]arene hybrid macrocyclic structures

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To reserve planar chirality, enhance molecular recognition, and build advanced self-assemblies, hybrid macrocyclic hosts containing rigid pillar[*n*]arene and flexible calix[*m*]arene were designed, prepared and investigated for interesting applications. This review summarizes and discusses different synthetic strategies for constructing hybrid macrocyclic structures. Pillar[*n*]arene dimer with rigid aromatic double bridges provided the possibility of introducing calix[*m*]arene cavities, where the planar chirality was reserved in the structure of pillararene. The capacity for molecular recognition was enhanced by hybrid macrocyclic cavities. Interestingly, the obtained pillar[*n*]arene–calix[*m*]arene could self-assemble into “channels” and “honeycomb” in both the solid state and solution phase as well as donate the molecular architecture as the wheel for the formation of mechanically interlocked molecules, such as rotaxane. In addition, the pillar[*n*]arene and calix[*m*]arene could also be coupled together to produce pillar[*n*]arene embedded 1,3-alternate and cone conformational calix[*m*]arene derivatives, which could catalyze the oxidative polymerization of aniline in aqueous solutions. Except for building hybrid cyclophanes by covalent bonds, weak supramolecular interactions were used to prepare pillar[*n*]arene–calix[*m*]arene analogous composites with other pillar-like pillar[*n*]pyridiniums and calix-like calix[*m*]pyrroles, exhibiting reasonable performances in enhancing molecular recognition and trapping solvent molecules.

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1 Introduction

To mimic natural and biological processes,^{1–3} such as protein–glucose interactions,^{4–8} macrocycles^{9–11} were designed and prepared as specialized host molecules^{12,13} for molecular

recognition¹⁴ by weak supramolecular interactions.¹⁵ To date, various macrocycles^{16–18} with various physiochemical characteristics have been reported. Among them, cyclophanes^{19–21} with repeated aromatic moieties, such as pillar[*n*]arene^{22–28} and calix[*m*]arene^{29–34} (Scheme 1), have attracted considerable academic and practical attention.³⁵ For example, owing to the presence of multivalent modification sites,³⁶ the structural skeletons of both pillar[*n*]arene and calix[*m*]arene could be directly used as the backbone for embedding valuable functional groups for various applications to water-soluble³⁷ self-assembled amphiphiles,^{38–41}

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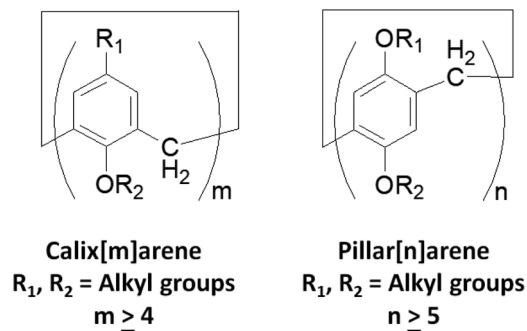

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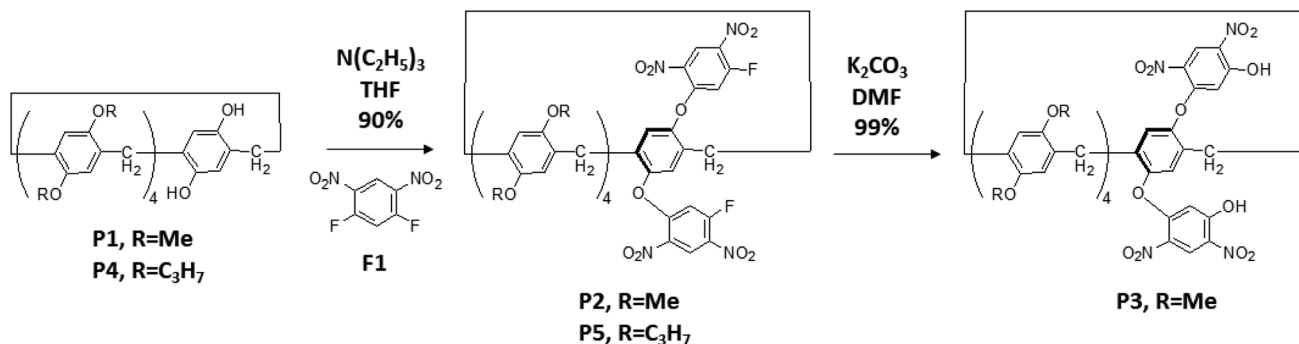
Scheme 1 Schematic presentation of the structures of pillar[n]arene and calix[m]arene.

advanced hierarchical architectures,^{42,43} such as metal organic frameworks,^{44–48} as well as energy storage and batteries.^{49,50}

Actually, owing to the presence of similar aromatic oligomeric structures, the development of novel structures and applications of pillar[n]arene⁵¹ has always resembled those of calix[m]arene.⁵² However, because of different substitution sites on aromatic rings, pillar[n]arene and calix[m]arene⁵³ always exhibit different topologies and morphologies in molecular

conformation and configuration,⁵⁴ as well as diverse behaviors in particular physiochemical characteristics.⁵⁵ For example, from the molecular geometry and shape perspective, the flexible structures of calix[m]arene could result in an adaptable cavity for diverse guests,⁵⁶ while the rigid conformational structures of pillar[n]arene can produce unique planar chirality.⁵⁷

It is important to compare these two attractive analogues of aromatic macrocycles in terms of their structural and physiochemical behaviors.⁵⁸ Several investigation methods have been developed for this purpose; for example, computational studies⁵⁹ such as density functional theory (DFT)⁶⁰ have been employed in investigating the diverse physiochemical properties of pillar[n]arene and calix[m]arene for different performances and applications, such as host–guest complexation.⁶⁰ Furthermore, a direct comparison between these two cyclophanes in practical experiments was also carried out.^{61,62} Pillar[n]arene and calix[m]arene demonstrated their advantages. Thus, it aroused another academic interest in combining the molecular structure and characteristics of pillar[n]arene and calix[m]arene with the art of organic synthesis.⁶³ The integration of pillar[n]arene and calix[m]arene into hybrid host molecules not only enriches the family of hybrid macrocycles but also



Scheme 2 The synthetic strategy that produces a significant previous piece of P2/P5 and P3 in high yields using the nucleophilic substitution of P1/P4 with F1.⁸⁵



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functional hybrid materials, as well as metal ligated materials.



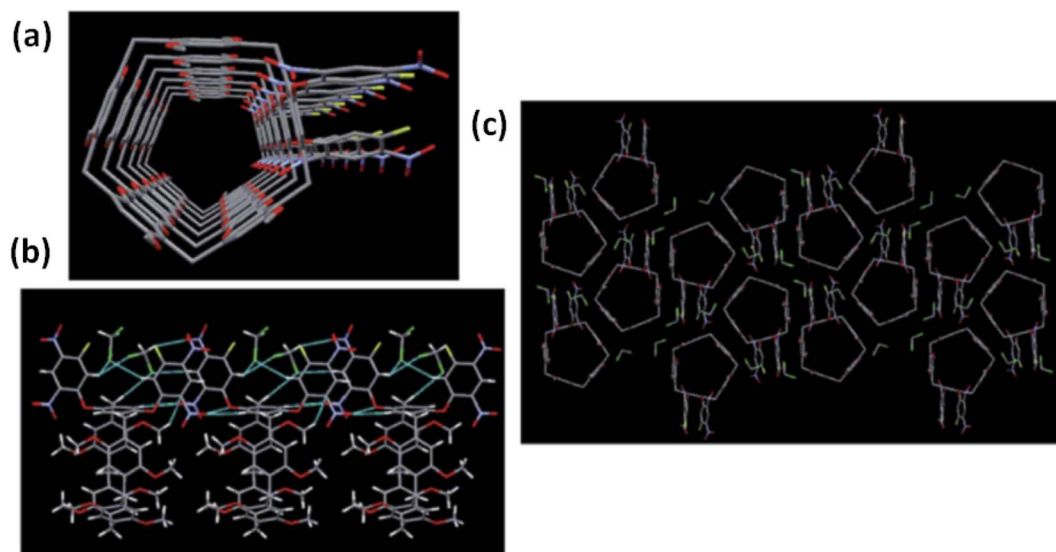
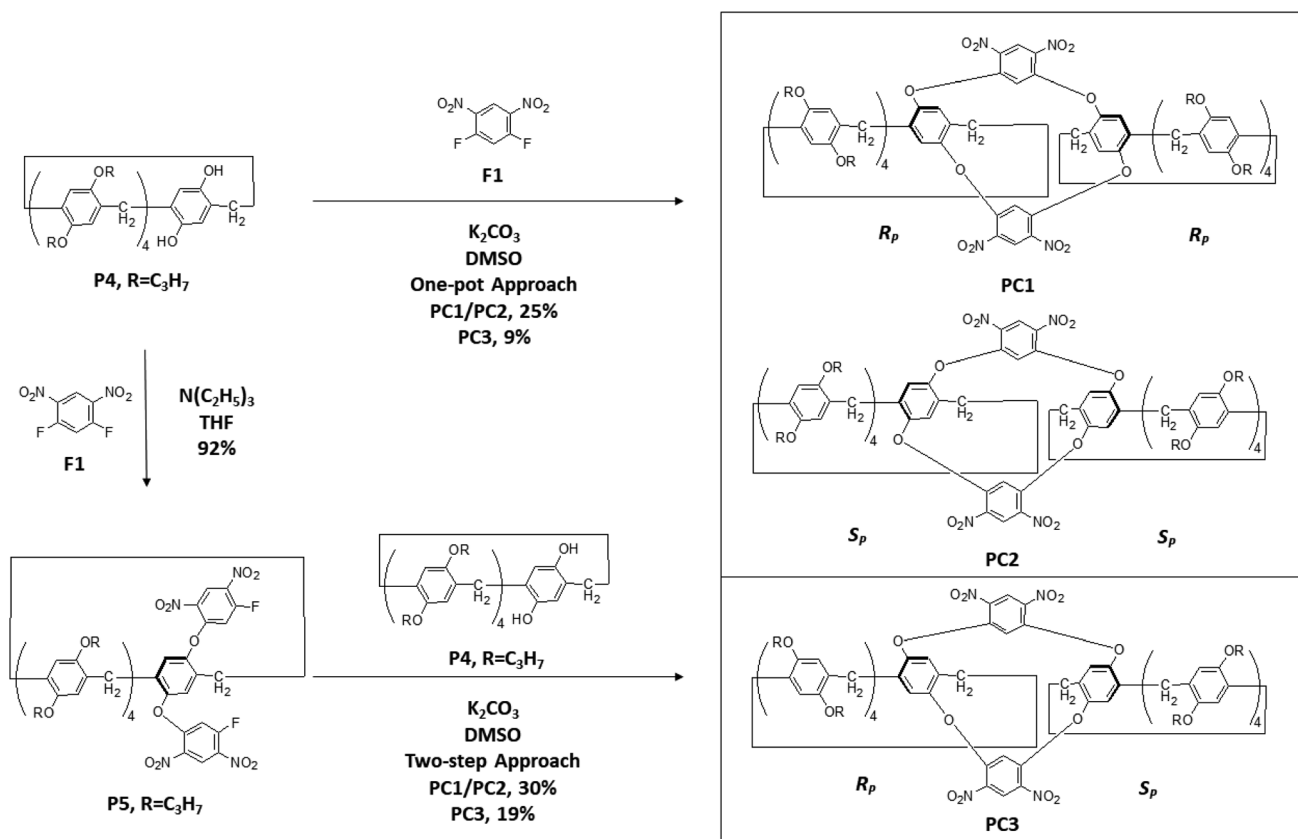


Fig. 1 Single crystal structures of P2 in stick representation indicate (a) a column-like tubular supramolecular self-assembly with (b) noncovalent interactions, as highlighted in green, as well as (c) honeycombed self-assemblies owing to the possession of π - π stacking interactions and C-H $\cdots\pi$ hydrogen bonds, where hydrogen atoms were omitted for clarity.⁶⁵

combines their features, such as flexible architectures and planar chirality.^{64–67}

In this review, the preparation and application of pillar[*n*]arene-calix[*m*]arene hybrid macrocyclic compounds are

summarized and discussed. Different classic organic synthesis methods⁶⁸ were employed during the preparation, producing pillar[*n*]arene dimer with aromatic double bridges, coupled with pillar[*n*]arene-calix[*m*]arene hybrid hosts, and noncovalent



Scheme 3 Two synthesis routes from the starting molecule P4 with the assistance of F1 to prepare diverse oxacalix[4]arene-bridged pillar[5]arene dimers, such as PC1, PC2 and PC3, with different planar chirality. P5 is an important intermediate compound in one synthesis strategy.⁶⁵



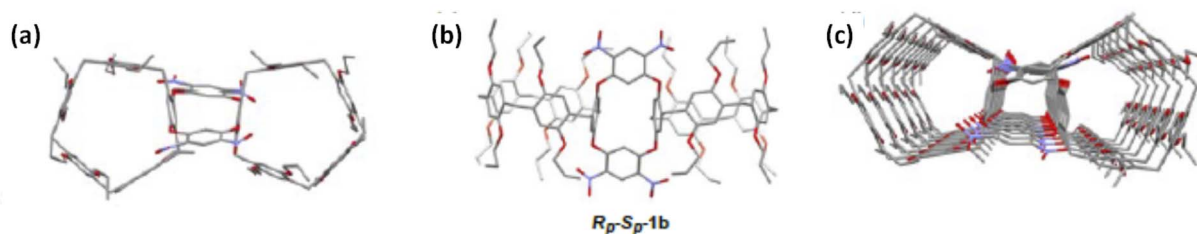


Fig. 2 Single crystal structures of PC3 in the stick representation of (a) top view, (b) side view and (c) packing model showing a self-assembled channel-like architecture. The configurations of the two pillar[5]arenes possessed R_p and S_p rings. Solvent molecules and hydrogen atoms were omitted for clarity.⁸⁵

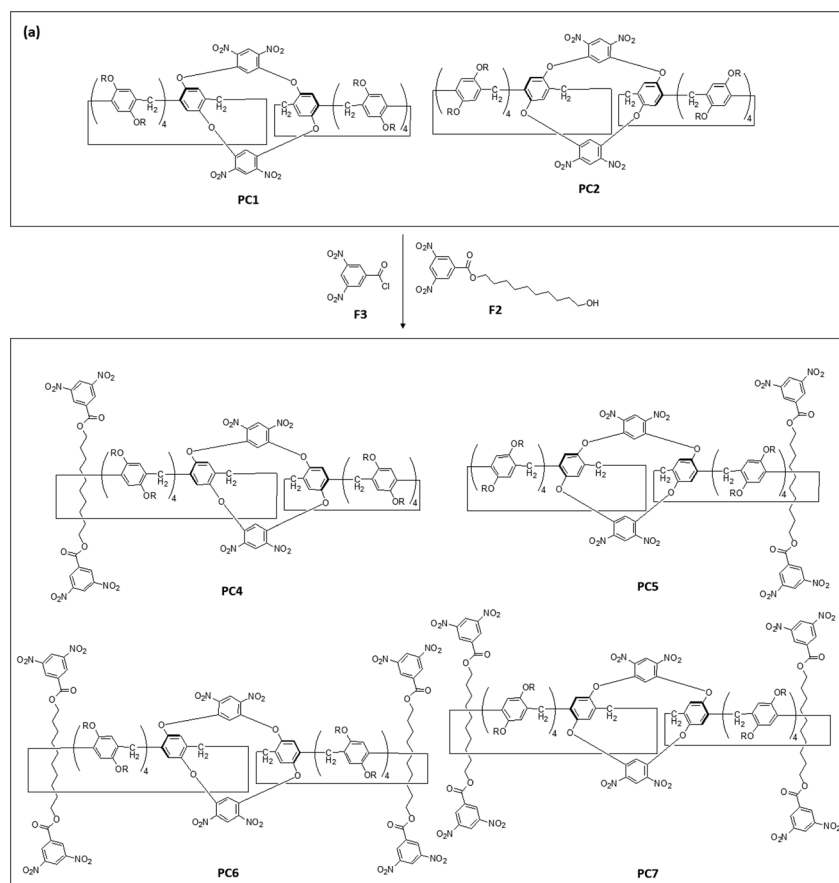
interaction-based pillar[n]arene–calix[m]arene resembling systems. Pillar[n]arene dimer with rigid aromatic double bridges possessing resembled calix[m]arene cavities could reserve the planar chirality and include dumbbell guests^{69,70} for fabricating mechanically interlocked molecules.^{71,72} In addition, the pillar[n]arene and calix[m]arene could also be covalently coupled to produce pillar[n]arene-containing 1,3-alternate and cone conformational calix[m]arene derivatives for catalyzing the oxidative polymerization of aniline.⁷³ Furthermore, weak supramolecular interactions have been used to prepare pillar[n]arene–calix[m]arene analogous composites using pillar[n]pyridiniums⁷⁴/calixarene and calix[m]pyrrole^{75,76}/pillararene to

enhance molecular recognition and trapping solvent molecules.⁷⁷ Finally, we consider possible scientific and technical issues and new challenges, as well as provide brief and primary suggestions for future studies to be conducted on pillar[n]arene–calix[m]arene hybrid macrocyclic structures.

2 Preparation of pillar[n]arene–calix[m]arene hybrid macrocyclic structures

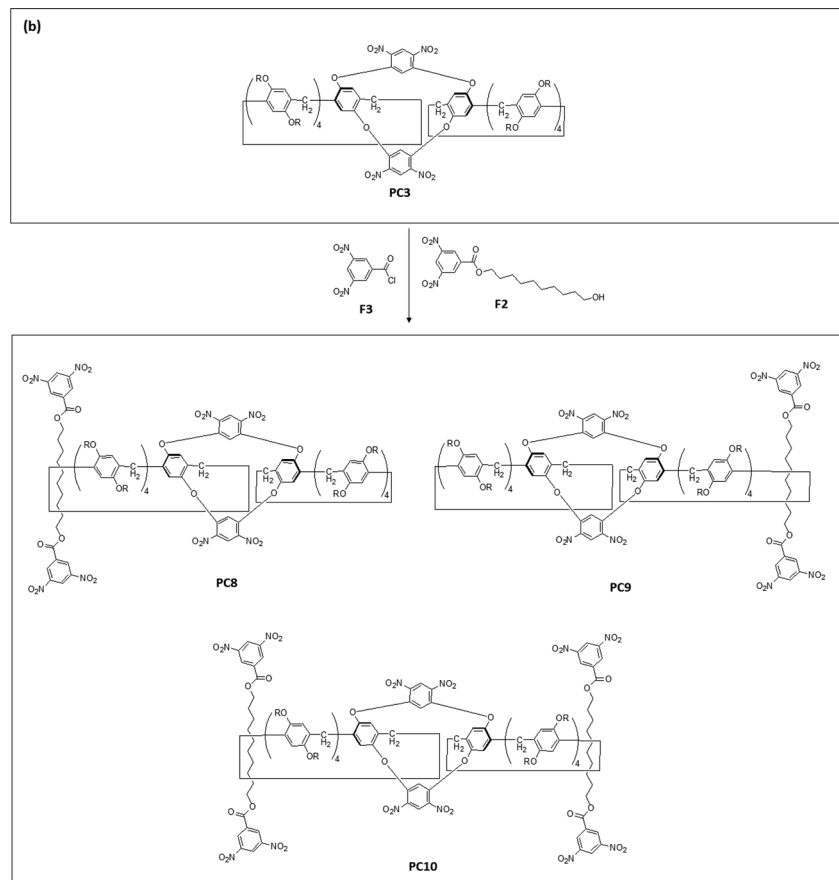
2.1 Merging structures of pillar[n]arene and calix[m]arene

Based on the art of organic synthesis,⁷⁸ both the direct modification of pillar[n]arene with calix[m]arene and the



Scheme 4 Schematic illustration of the synthesis of diverse planar chirality-containing pillar[5]arene-based [2]rotaxanes, such as PC4, PC5, PC8 and PC9, as well as [3]rotaxanes, such as PC6, PC7 and PC10, by utilizing previous pieces, such as double-bridged pillar[5]arene derivatives, including PC1, PC2 and PC3, as well as functional reagents, including stopper-containing F2 and F3 for the formation of axle subunits.⁸⁵





Scheme 4 (contd.)

functionalization of calix[*n*]arene with pillar[*n*]arene were challenging because of several organic experimental issues, such as the diverse solubilities of the two cyclophanes in reaction solutions,⁷⁹ as well as the multivalent reactive sites⁸⁰ embedded in their structures. Thus, the current rigid skeleton of pillar[*n*]arene was initially considered the structural basis, and heteroatoms, such as oxygen-atom on the hydroquinone moieties of pillar[*n*]arene, were further used as a bridge to incorporate extra aromatic subunits *via* meta positions, producing an additional calix-like cyclophane cavity. Such hybrid macrocycles have particular structural characteristics, *e.g.*, “fused” hybrid macrocyclic cavities “double-bridged”⁸¹ by aromatic rigid linkers with unique planar chirality.⁸² Furthermore, it provides the opportunity to raise another supramolecular issue, *i.e.*, the fabrication of mechanically interlocked molecules.⁸²

For example,⁸³ 1,4-dimethoxypillar[4]arene[1]hydroquinone **P1** (Scheme 2) was used as the previous piece to react with the “bridging group”—1,5-difluoro-2,4-dinitrobenzene **F1** (Scheme 2) in the presence of triethylamine as the catalyst in THF solutions under N₂ atmosphere to produce 2,4-dinitro-5-fluorophenyl difunctionalized pillar[5]arene **P2** (Scheme 2) using the classic nucleophilic aromatic substitution (S_NAr) yielding 90%. Then, **P2** was dissolved in DMF to promote its solubility under K₂CO₃ condition and prepare another nitrophenyl difunctionalized pillar[5]arene **P3** (Scheme 2), yielding 99%. Interestingly,

the vapor diffusion method was applied to synthesize the single crystal structures of **P2** and **P3** using hexane, heptane and dichloromethane, revealing that tubular and honeycombed self-assemblies⁸⁴ were formed in the solid state with solvent molecules encapsulated inside these structures (Fig. 1).⁸³

Considering the above organic experiment of preparing significant previous pieces of conformationally locked A1/A2 difunctionalized pillar[5]arene **P2** and **P3** (Scheme 2), the pillar[5]arene/calix[4]arene-containing fused hybrid macrocyclic compound—oxacalix[4]arene-bridged pillar[5]arene dimers **PC1–PC3** with diverse planar chirality (Scheme 3) were further obtained using two different synthesis strategies, such as the

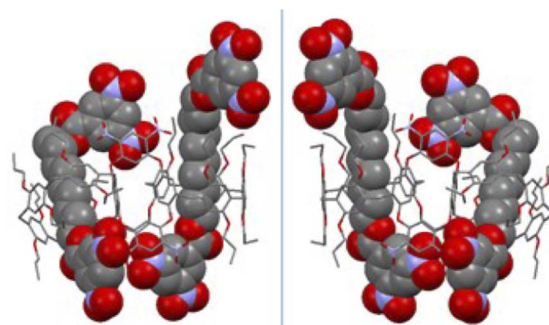
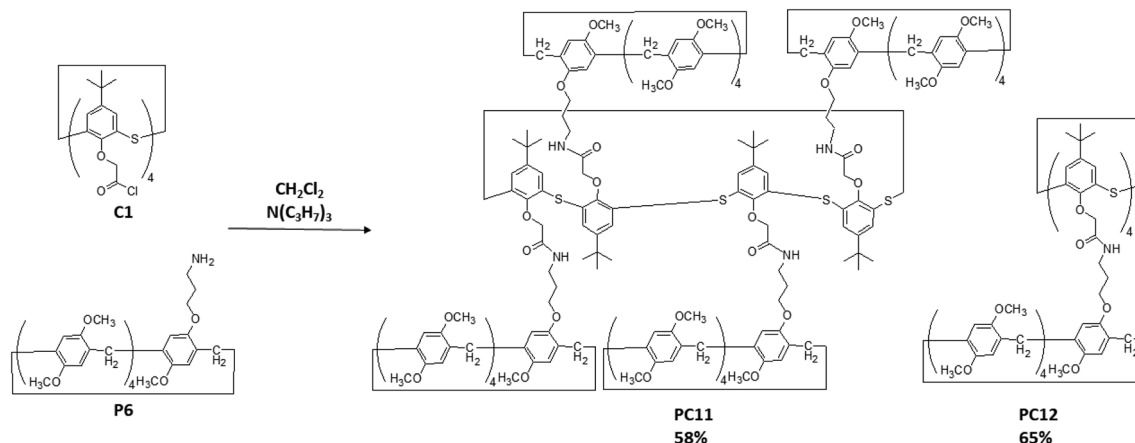


Fig. 3 Single crystal structures of a pair of planar chiral enantiomers, PC6 and PC7. Hydrogen atoms were omitted for clarity.⁸⁵





Scheme 5 Synthesis route for producing PC11 and PC12 by coupling thiocalix[4]arene C1 and pillar[5]arene P6.⁸⁸

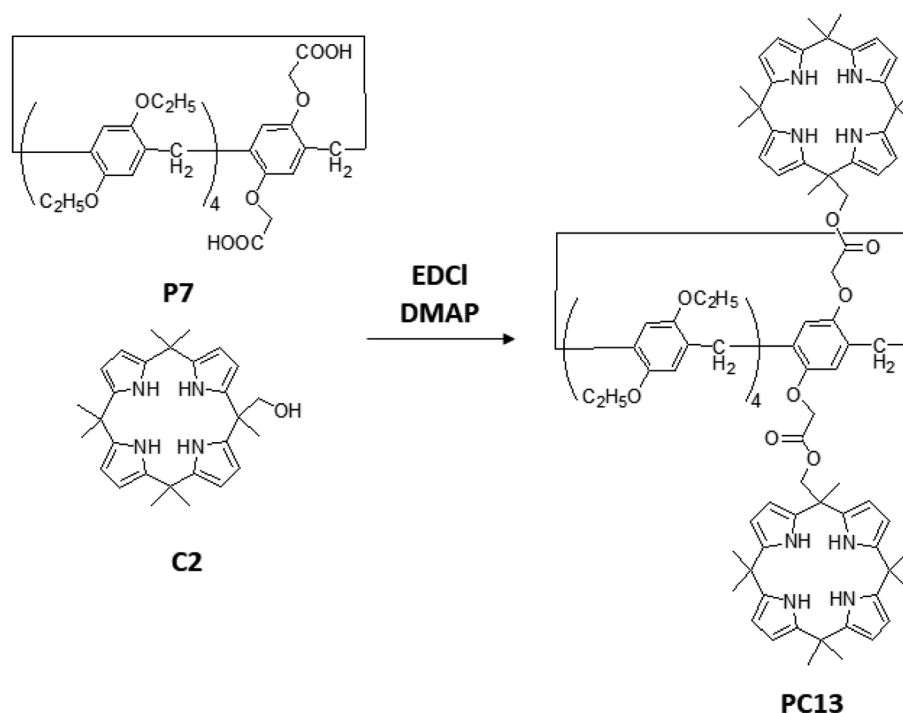
one-pot reaction between pillar[4]arene[1]hydroquinone P4 and F1 (Scheme 3) in DMSO in the presence of K_2CO_3 at room temperature and two-step approach with P5 (Scheme 3) as the intermediate compound in relatively improved yields.⁸⁵ Interestingly, PC1 and PC2 were a pair of enantiomers, as confirmed by chiral high performance liquid chromatography (HPLC), and PC3 (Fig. 2) was the achiral *meso* compound of PC1/PC2 as revealed by 1H NMR and electrospray ionization high resolution mass spectrometry (ESI-HRMS).

Fused hybrid macrocyclic hosts are good candidates for preparing advanced molecular architectures, such as mechanically interlocked molecules. Conformationally fixed double-bridged pillar[5]arene-calix[4]arene hybrid structures were

further used as the “wheel” subunit for constructing planar chirality-containing [2]rotaxanes,^{86,87} such as PC4, PC5, PC8 and PC9 (Scheme 4), as well as [3]rotaxanes, such as PC6, PC7 and PC10 (Scheme 4), using the “stopper” moieties-possessing functional molecules F2 and F3 (Scheme 4) to form the “axle” subunit *via* the threading/stoppering method (Fig. 3).⁸⁵

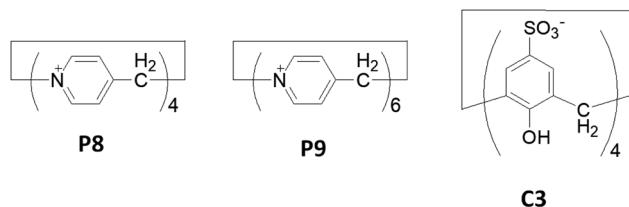
2.2 Coupling independent structures of pillar[*n*]arene and calix[*m*]arene

Except for expanding the current structural skeleton of pillar[*n*]arene to build extra calix-like cavities, two independent structures of pillar[*n*]arene and calix[*m*]arene can be coupled *via* classic organic reactions. For example, tetraacyl chlorides-



Scheme 6 Synthesis of PC13 using P7 and C2.⁹¹



Scheme 7 Chemical structures of P8, P9 and C3.⁹²

containing *p*-*tert*-butylthiacalix[4]arene **C1** (Scheme 5) could be integrated with amino monofunctionalized pillar[5]arene derivative **P6** (Scheme 5) in dichloromethane in the presence of Hünge's base under the argon atmosphere through acylation reaction, preparing pillar[5]arene–calix[4]arene hybrid macrocycles, such as 1,3-alternate conformational calixarene-containing **PC11** (Scheme 5) and cone conformational calixarene-containing **PC12** (Scheme 5), yielding 58% and 65%, respectively.⁸⁸ Interestingly, the combination of pillar[5]arene and thiacalix[4]arene into a hybrid macrocyclic system not only

allowed the integration of the diverse capacities of molecular recognition towards valuable guest molecules, such as aniline and aniline/*p*-toluenesulfonic acid, but also promoted the oxidative polymerization of aniline in aqueous *p*-toluenesulfonic acid solutions by increasing the yield and molecular weight of emeraldine.

2.3 Integrating pillar-like and calix-like aromatic cyclic oligomers

In addition to the direct coupling of pillar[*n*]arene and calix[*m*]arene into hybrid macrocyclic structures, other pillar-like and calix-like macrocycles, such as heteroatom-containing ones, were employed to resemble fused cyclophanes. Owing to the introduction of heteroatoms, the capacity for molecular recognition generated from fused macrocycles was enhanced.

For example, carboxylate^{89,90} difunctionalized pillar[5]arene **P7** (Scheme 6) was reacted with the calix-like nitrogen-rich macrocycle—calix[4]pyrrole **C2** (Scheme 6) *via* an esterification reaction in the presence of catalytic amounts of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride

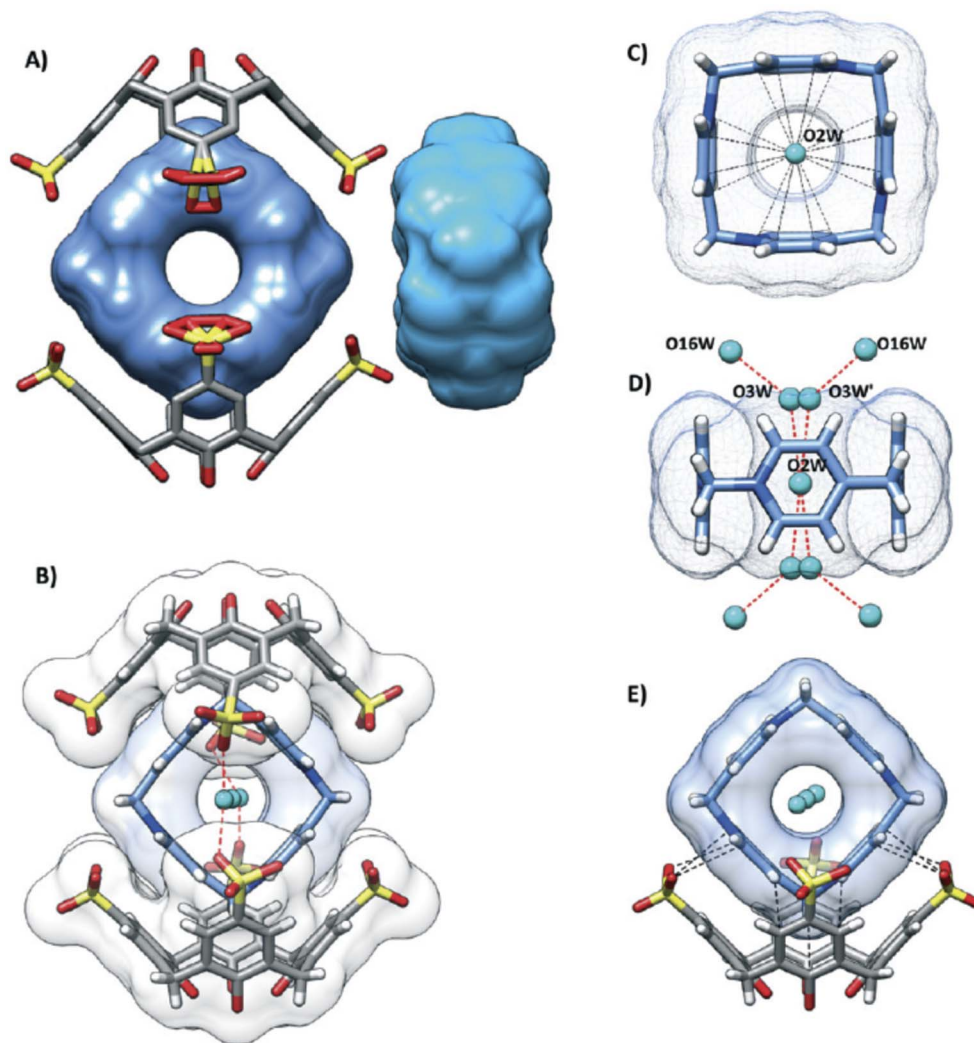


Fig. 4 Expanded asymmetric unit of 1/2 P8·C3 (A), where H₂O was trapped inside the center of P8 (B) by a series of weak supramolecular interactions (C–E).⁹² Copyright© 2022 by The Royal Society of Chemistry.



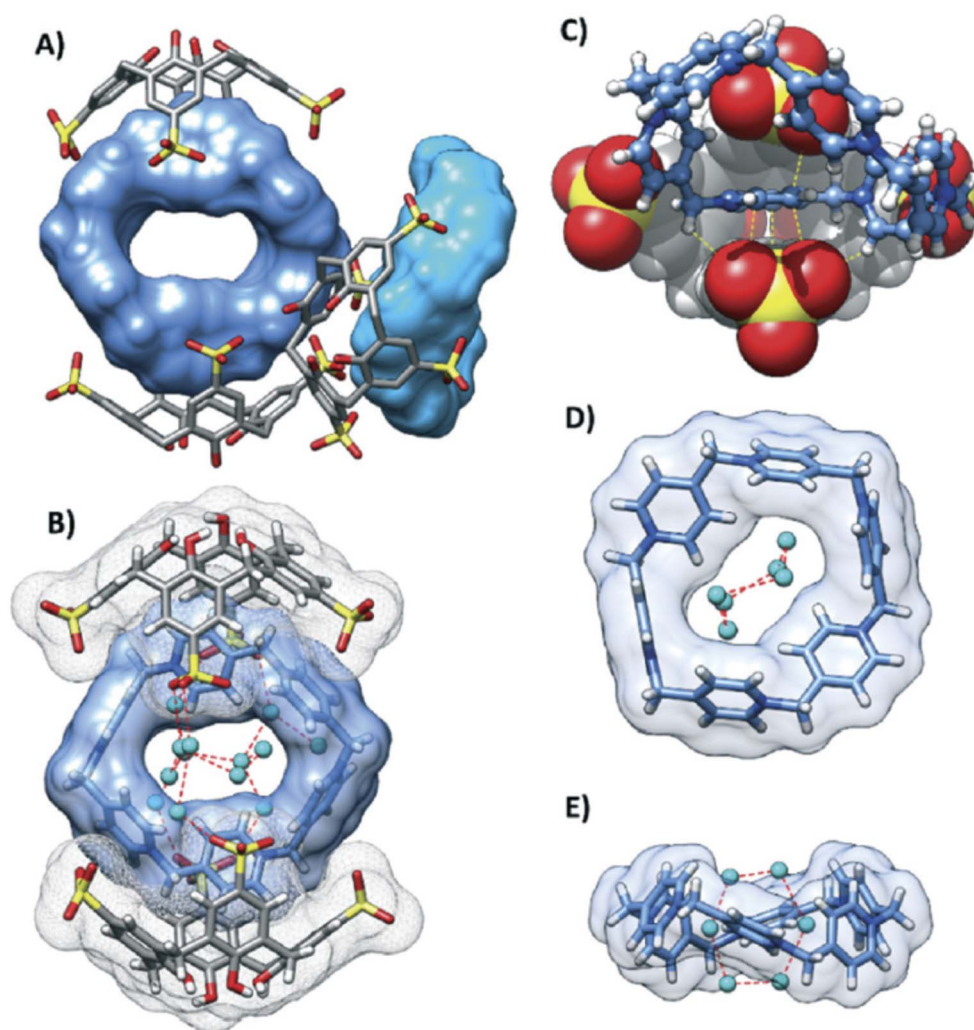


Fig. 5 Asymmetric unit of 1/2 P9·C3 (A), where H₂O was trapped inside P9 (B) by a series of weak supramolecular interactions (C–E).⁹² Copyright© 2022 by The Royal Society of Chemistry.

(EDCI) and 4-dimethylaminopyridine (DMAP), leading to the formation of pillar[5]arene-calix[4]pyrrole **PC13** (Scheme 6) with two calix[4]pyrrole subunits on both ends yielding 50%.⁹¹ Owing to the possession of nitrogen-rich calix[4]pyrrole structures and conformational fixed pillar[5]arene moieties, **PC13** exhibited enhanced inclusion ability for chiral anion salts, such as chiral (*R/S*)-mandelate anionic guests as tetramethylammonium salts, by a series of weak supramolecular interactions, including hydrogen bonding, cation- π , π - π stacking and C-H \cdots π interactions. The association constants (K_a) were determined in the range of 5.15×10^4 to $2.25 \times 10^5 \text{ M}^{-1}$.

Particularly, the introduction of heteroatoms embedded in the macrocyclic structures provided the possibility of combining pillar-like and calix-like cyclic aromatic oligomers *via* noncovalent interactions, *i.e.*, the heteroatom-containing macrocycles acting as the guest molecule to be included by the other cavity *via* supramolecular interactions, such as electrostatic forces. For example,⁹² cationic pillar[*n*]pyridiniums, such as the rigid square-shaped tetramer **P8** and the flexible roughly hexagonal hexamer **P9** (Scheme 7), were encapsulated

by anionic *p*-sulfonatocalix[4]arene **C3** (Scheme 7) in the solid state and aqueous solution phase by electrostatic attractions, and anion \cdots π^+ , anion \cdots $\pi^+\cdots$ anion and $\pi\cdots\pi^+$ interactions, leading to the co-assemblies of oppositely charged hybrid macrocycles (Fig. 4 and 5).

3 Overview and outlook

In conclusion, the design, preparation and application of pillar [*n*]arene-calix[*m*]arene hybrid macrocyclic structures were discussed and summarized in this review. To overcome the challenges of the art of organic synthesis, various strategies were employed to fabricate hybrid cyclophanes. First, the structural skeletons of pillar[*n*]arene and calix[*m*]arene were fused *via* the formation of a pillararene dimer⁹³ with double aromatic bridges by incorporating the architectures of calixarene under the S_NAr reaction conditions, leading to the self-assembly of hybrid macrocycles in the solid and solution phases, the reservation of planar chirality of pillararene, and the enhancement of molecular recognition by hybrid cavities. Interestingly, double-



bridged pillar[*n*]arene dimers further provided the pillar[*n*]arene cavity as the wheel to integrate with “dumb-bell”-like linear molecules, affording mechanically interlocked molecules, such as [2]/[3]rotaxanes, with planar chirality. Additionally, classic organic synthetic methods, such as acylation reaction, were further carried out to directly combine independent units of pillar[*n*]arene and calix[*m*]arene, producing two types of pillar[5]arene–calix[4]arene hybrid macrocycles with 1,3-alternate and cone conformations, which were observed to have the capacity to catalyze the oxidative polymerization of aniline in aqueous solutions. Furthermore, pillar-like cyclophanes, such as pillar[*n*]pyridiniums, and calix-like cyclophanes, such as calix[*m*]pyrrole, were also used for the fabrication of hybrid macrocyclic systems with calixarene and pillararene, respectively, to resemble pillar[*n*]arene–calix[*m*]arene composites, where both covalent bonds and noncovalent interactions acted as the driving forces. Particularly, these analogous systems exhibited reasonable performances in enhancing molecular recognition and trapping solvent molecules in the solution and solid phases.

Numerous studies on the fabrication and application of pillararene–calixarene hybrid macrocycles are still attractive for future researchers, needing attention from related scientists in synthesis chemistry, physical chemistry and material science.

First, the efficient integration of pillar[*n*]arene and calix[*m*]arene together as well as the effective separation of enantiopure hybrid macrocycles⁹⁴ are still challenges in organic synthesis chemistry. In particular, owing to the possession of pillararene and the introduction of larger functional groups, the planar chirality of pillararene granted future applications for hybrid macrocycles but made the separation and purification of such compounds more difficult.⁹⁵

Second, other sized pillar-like and calix-like aromatic macrocycles should be employed in the fabrication of such hybrid cyclophanes to enrich the family of pillar[*n*]arene/calix[*m*]arene-based fused cyclophanes.⁹⁶ Larger cavities of fused hybrid macrocycles not only enlarge the possibilities of complexing diverse functional guest molecules,⁹⁷ but also provide significant backbones and building blocks for constructing advanced functional structures, such as self-assemblies and mechanically interlocked molecules.^{98,99} Future applications should be further explored based on functional architectures with covalent bonds, mechanical forces and supramolecular interactions.¹⁰⁰

Third, a computational study is highly recommended for proposing and investigating pillararene–calixarene hybrid macrocycle-based supramolecular materials,^{101,102} such as the study of different behaviors of host–guest inclusions, as well as the competition and cooperation between the two hybrid macrocycles.¹⁰³

Abbreviations

EDCI	1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride
ESI-	Electrospray ionization high resolution mass spectrometry
HRMS	

DMAP	4-Dimethylaminopyridine
HPLC	High performance liquid chromatography
K_a	Association constants
S_NAr	Nucleophilic aromatic substitution

Conflicts of interest

There are no conflicts to declare.

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