doi:10.2533/chimia.2016.61 Chimia 70 (2016) 61–66 © Swiss Chemical Society

# From Pillar[*n*]arene Scaffolds for the Preparation of Nanomaterials to Pillar[5]arene-containing Rotaxanes

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*Abstract:* Pillar[*n*]arenes are a new class of macrocycles that are efficiently prepared from readily available building blocks. In this particular field, our research teams became interested in the use of a pillar[5]arene core as a compact scaffold for the synthesis of nanomaterials with a controlled distribution of functional groups on both rims of the macrocyclic framework. Such compounds have found applications in biology as multivalent ligands for specific lectines or as polycationic compounds for gene delivery. Liquid-crystalline derivatives have been prepared by grafting mesogenic subunits on the pillar[5]arene core. On the other hand, we also became interested in the preparation of pillar[5]arene-containing [2]rotaxanes. In particular, we have shown that pillar[5]arene-based [2]rotaxanes can be obtained from the reaction of amine stoppers with pseudo-rotaxanes resulting from the association of a pillar[5]arene derivative with a diacyl chloride reagent. Finally, amphiphilic [2]rotaxanes have been prepared and incorporated in thin ordered films at the air–water interface.

**Keywords:** Macrocycles · Nanomaterials · Pillar[n]arenes · Rotaxanes

## 1. Introduction

Macrocyclic compounds are playing a major role in the field of supramolecular chemistry.[1] Emblematic examples include crown-ethers,[2] cyclodextrins,[3] cucurbiturils,[4] cyclotriveratrylenes (CTV)[5] and calix[*n*]arenes.[6] Whereas CTVs and calix[*n*]arenes have been known for decades, their *para*-cyclophane analogues, namely pillar[*n*]arenes (*n* = 5 or 6), were discovered only recently (Fig. 1).[7] Pillar[*n*]arenes are composed of 1,4-disubstituted hydroquinone subunits linked by methylene bridges in their 2,5-positions.[7] Whereas CTV and calix[*n*]arenes adopt generally cone-shaped conformations, pillar[*n*]arenes are symmetrical tubular-shaped compounds with two identical rims.

Following the first report in 2008, pillar[*n*]arenes have attracted significant efforts focused on both the optimization of their preparation and their incorporation in supramolecular ensembles.[8] Despite their recent discovery, pillar[*n*]arenes are already at the forefront of supramolecular chemistry.[8] As part of this research, our teams became interested in the use of a pillar[5]arene core as a compact scaffold for the preparation of nanomaterials with a controlled distribution of functional groups on the macrocyclic framework. On the other hand, we also became interested in the preparation of pillar[5]arene-containing [2]rotaxanes. These results are summarized in the present account together with general considerations concerning the synthesis and the conformation of pillar[5]arenes.

## 2. Synthesis and Conformation of Pillar[*n*]arenes

Concerning their synthesis, pillar[*n*]arenes are usually prepared in good yields from 1,4-dialkoxybenzene and paraformaldehyde in the presence of $BF_3Et_2O$ (Scheme 1).[9] When the reaction is performed in $CH_2Cl_2$ or 1,2-dichloroethane, the cyclopentamer (*n* = 5) is the only product of cyclization;[9] in a few cases however the cyclohexamer (*n* = 6) is also produced but always as a minor product and in rather low yields.[9] In contrast, the preferential preparation of pillar[6]arenes is observed when the reaction between 1,4-dialkoxybenzene and paraformaldehyde is carried out in $CHCl_3$ with $FeCl_3$ as the Lewis acid catalyst.[10] The latter observations suggest that the solvent molecules are somehow templating the cyclization leading to the cyclooligomers. In other words, the outcome of the reaction is related to the affinity of the pillar[*n*]arene derivative for the solvent.[11]

Moreover, it has been shown that the cyclooligomerization is thermodynami-

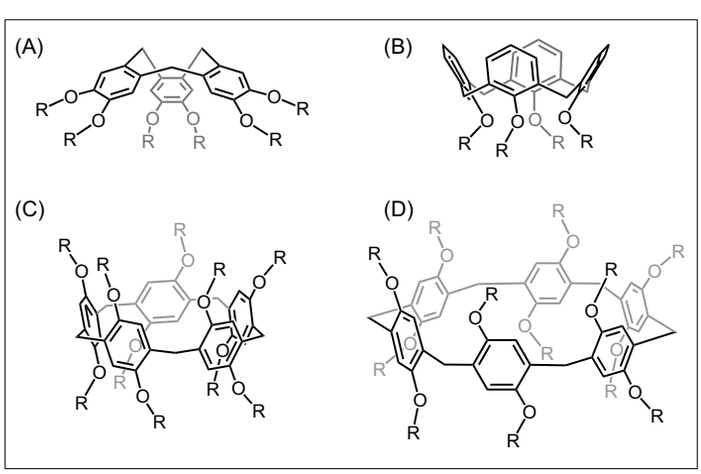


Fig. 1. (A) Cyclotriveratrylene; (B) calix[4]arene; (C) pillar[5]arene; (D) pillar[6]arene.

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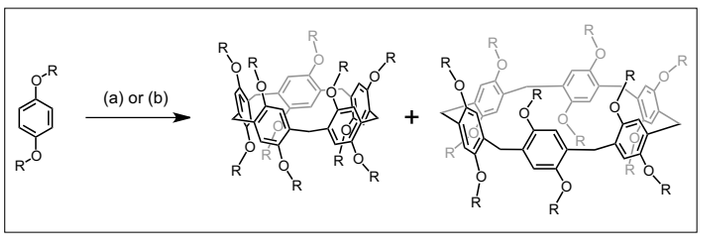



Scheme 1. Typical conditions for the synthesis of pillar[5] and pillar[6] arenes. *Reagents and conditions*: (a) $(CH_2O)_n$, $BF_3Et_2O$, $CH_2ClCH_2Cl$, r.t. (pillar[5]arene: 30–60%, pillar[6]arene: traces); (b) $(CH_2O)_n$, $FeCl_3$, $CHCl_3$, 45 °C (pillar[5]arene: 10–30%, pillar[6]arene: 20–40%).

cally driven owing to the reversibility of the Friedel-Crafts reaction, thus explaining the high yielding synthesis of pillar[*n*]arenes.[12] Finally, when the cyclization reaction is performed under kinetic control, it is possible to obtain larger pillar[*n*]arenes ($n$ = 7–10).[13] The largest members of this family of macrocycles remain however exotic species and the main part of the work done in the field of pillar[*n*]arenes involves cyclopentamers and cyclohexamers.[8]

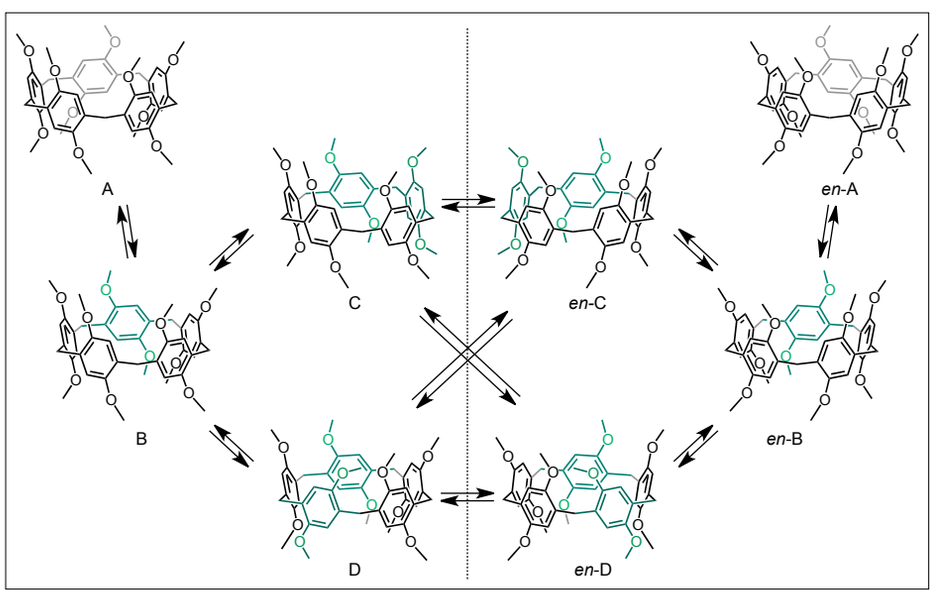
One of the features of pillar[*n*]arenes that differs from other classical macrocycles is related to their planar chirality resulting from the position of the alkoxy substituents (Scheme 2). When the alkyl group is small enough, oxygen-through-the-annulus movements of the hydroquinone units are possible.[14] In the case of the cyclopentamer, there are in principle eight possible conformers (actually four pairs of enantiomers) depending on the relative orientation of the OR subunits. However, for steric reasons, the $D_5$-symmetrical conformers (A and *en*-A) are largely favored. When the alkoxy group is large enough to prevent the rotation of the hydroquinone subunits, the Friedel-Crafts reaction provides almost exclusively pillar[*n*]arenes with a $D_n$ symmetry. In the particular case of percyclohexylmethyl-pillar[5]arene, the enantiomers have been separated by chiral HPLC.[15]

As shown in Scheme 3, nonsymmetrical pillar[5]arenes have been prepared from nonsymmetrical 1,4-dialkoxybenzene monomers (*i.e.* substituted with two different alkoxy units). The cyclopentameric product is obtained as a mixture of four constitutional isomers that were separated by tedious chromatographic separations in some cases.[16] The co-cyclization from two distinct monomers has been also investigated.[17] In this case, eight cyclization products are possible and their relative proportions depend on the relative ratio of the two starting monomers. The preparation of pillar[5]arene derivatives bearing different groups is actually limited due to the formation of mixtures of products and new synthetic methods allowing for the preparation of selected isomers are clearly needed.

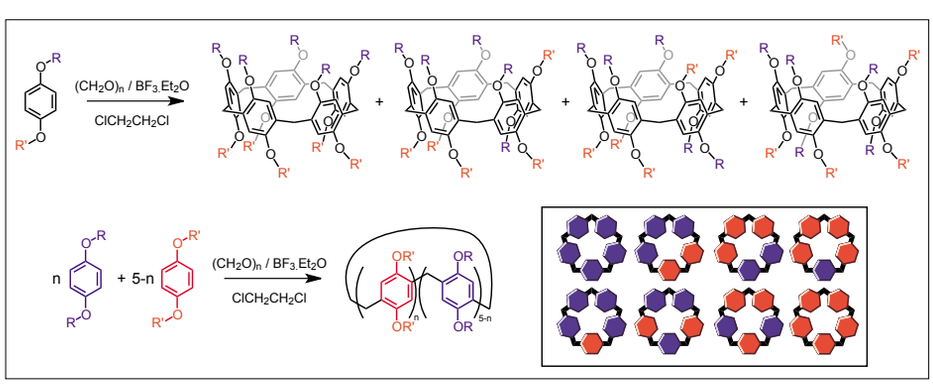
## 3. Pillar[*n*]arenes as Scaffolds for the Preparation of Nanomaterials

Owing to the presence of ten peripheral substituents, pillar[5]arene is an attractive platform for the preparation of nanomaterials with a controlled distribution of functional groups on the macrocyclic framework.[18] As already discussed, pillar[5]arenes are usually prepared from 1,4-dialkoxybenzene derivatives and paraformaldehyde in the presence of a Lewis acid catalyst.[8] The compatibility of these reaction conditions with other functional groups is quite limited and the direct preparation of pillar[5]arenes bearing sophisticated substituents is generally not possible. The cyclization reaction is also sensitive to the size of the substituents of the starting 1,4-dialkoxybenzene and the presence of large groups considerably reduces the yields.[8] These major problems have been solved by preparing readily available pillar[5]arene derivatives bearing peripheral reactive groups allowing the grafting of ten terminal subunits to generate sophisticated multifunctional molecular ensembles (Schemes 4 and 5).[18–20]

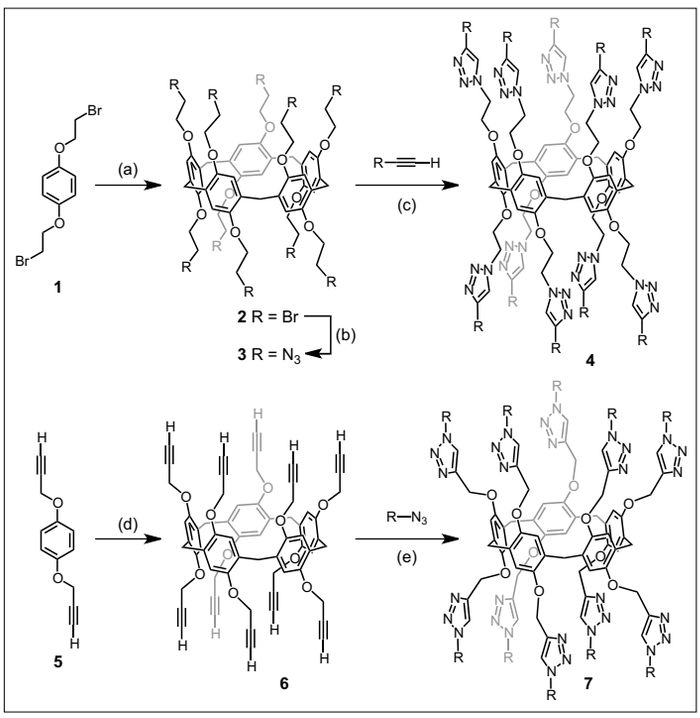
Building block **6** has been already used to produce polycationic derivatives for transfection experiments.[20] As shown in Scheme 5, the grafting of dendrons with peripheral Boc-protected amine groups onto a preconstructed pillar[5]arene scaf-




Scheme 2. All possible conformers of a pillar[5]arene derivative (four pairs of enantiomers, A: $D_5$-symmetric; B, C and D: $C_2$-symmetric). For steric reasons, the $D_5$-symmetrical conformers (A and *en*-A) are largely favored but racemization is observed when the alkoxy substituents are small enough to allow oxygen-through-the-annulus movements.




Scheme 3. Top: the preparation of pillar[5]arenes from nonsymmetrical monomers leads to four constitutional isomers. Bottom: the co-cyclization from two distinct monomers provides a mixture of eight cyclization products.

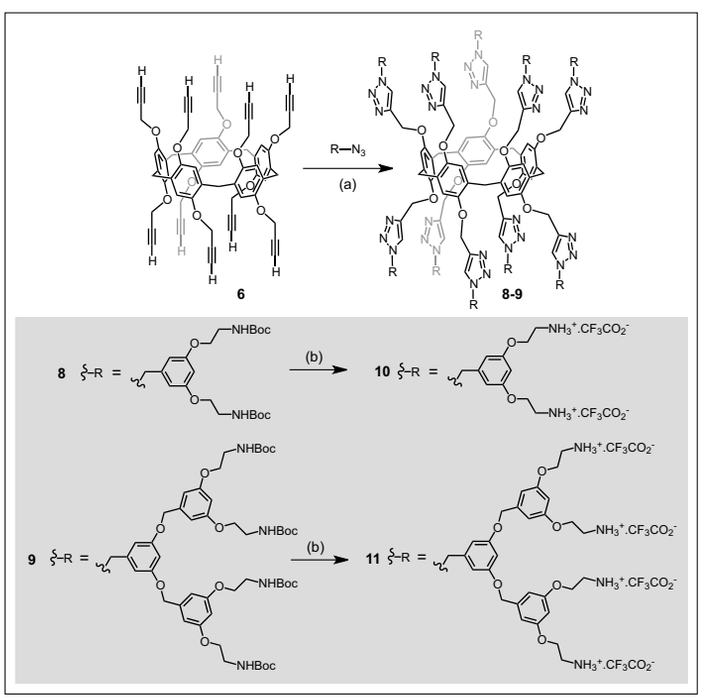


Scheme 4. Clickable pillar[5]arene scaffolds developed in our group. *Reagents and conditions*: (a) $BF_3Et_2O$, $(CH_2O)_n$, $ClCH_2CH_2Cl$ (60%); (b) $NaN_3$, DMF (98%); (c) $CuSO_4{\cdot}5H_2O$, sodium ascorbate, $CH_2Cl_2/H_2O$; (d) $BF_3Et_2O$, $(CH_2O)_n$, $ClCH_2CH_2Cl$ (40%); (e) $CuSO_4{\cdot}5H_2O$, sodium ascorbate, $CH_2Cl_2/H_2O$.

fold provided dendritic pillar[5]arene derivatives **8** and **9**. Upon treatment with TFA, water-soluble pillar[5]arenes **10** and **11** with 20 and 40 terminal ammonium subunits, respectively, have been obtained.

Stable nanoparticles have been obtained from plasmid DNA and polycationic compounds **10** and **11**. This has been demonstrated by several techniques such as gel electrophoresis, transmission electron microscopy (TEM) and dynamic light scattering (DLS) investigations. Transfection efficiencies of the self-assembled **10**/pCMV-Luc and **11**/pCMV-Luc polyplexes have been evaluated *in vitro* with HeLa cells (pCMV-Luc: luciferase plasmid). For both **10** and **11**, the transfection efficiencies are good even if slightly lower than that of the 'golden standard' JET-PEI™ (commercially available gene delivery system developed by Polyplus-Transfection, Illkirch, France). However, both pillar[5]arene derivatives are by far less toxic than JET-PEI™ .

In collaboration with Prof. Stéphane P. Vincent (Namur, Belgium), the pillar[5]arene scaffold has been used as a central core unit to prepare multivalent glycoconjugates (Fig. 2). Mannosylated pillar[5]arene derivative **12** has been assayed as an inhibitor of the adhesion of an uropathogenic *Escherichia coli* strain to red blood cells.[21] A single glycopillar[5]arene molecule can accommodate several FimH subunits and compound **12** displayed significantly higher inhibition levels than an appropriate monomeric compound in the hemagglutination inhibition assays. Following these first examples of glycopillar[5]arenes, other derivatives have been reported by the group of Huang.[22]



Scheme 5. Preparation of polycationic pillar[5]arene derivatives from building block **6**. *Reagents and conditions*: (a) $CuSO_4.5H_2O$, sodium ascorbate, $CH_2Cl_2/H_2O$ (**8**: 88%, **9**: 81%); (b) TFA (**10**: quantitative, **11**: quantitative).

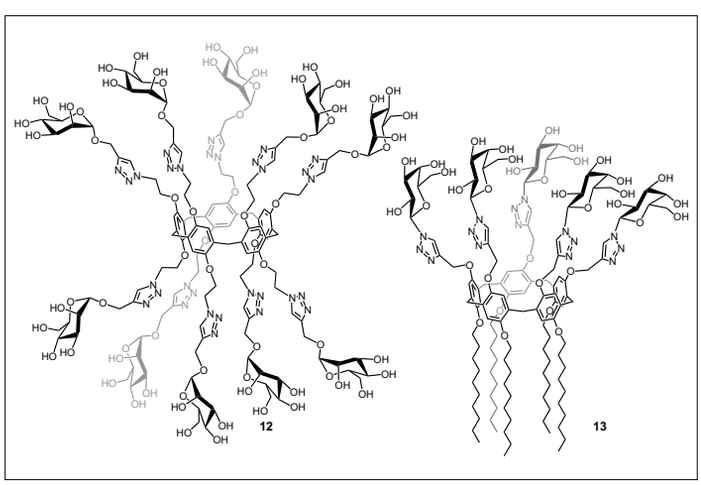


Fig. 2. Glycoconjugates **12** and **13**.

Amphiphilic pillar[5]arene **13** containing five galactose subunits on one rim and five alkyl chains on the other one have been prepared.[10] This amphiphilic compound forms nanotubular structures in water. These self-assembled nanostructures have been used as cell glues to agglutinate *Escherichia coli*.

Clickable pillar[*n*]arene ($n$ = 5 or 6) building blocks bearing peripheral azide functions have been also decorated with cyanobiphenyl moieties to provide the first examples of liquid-crystalline pillar[*n*]arene derivatives (compounds **15** and **16**, Fig. 3).[18,23] Importantly, comparison of their mesomorphic properties with those of a model monomer revealed the dramatic influence of the macrocyclic core. Effectively, only a monotropic mesophase was observed for the model monomeric compound (**14**: I → SmA: 149 °C; SmA → Cr: 125 °C; I: isotropic liquid, SmA: smectic A phase, Cr: crystalline solid). In contrast, a broad enantiotropic mesophase was ob-

served by linking together five (**15**: $T_g$: 32 °C; SmA → I: 201 °C; $T_g$: glass transition temperature) or six (**16**: $T_g$: 28 °C; SmA → I: 209 °C) linear subunits through the central macrocyclic pillar[*n*]arene core. As a result of the specific orientation of the peripheral mesogenic cyanobiphenyl moieties grafted on the pillar[*n*]arene core, the system adopts a supramolecular organization in which each smectic layer is interdigitated with its two neighboring ones. In this way, intermolecular π–π interactions between neighboring cyanobiphenyl subunits are weaker in the bulk for the macrocyclic derivatives thus explaining the macrocyclic effect observed for compounds **15** and **16** when compared to the corresponding monomeric subunit (compound **14**).

More recently, a similar approach was used by Wang, Chen and co-workers to prepare pillar[5]arene liquid-crystalline materials incorporating azobenzene subunits (compounds **17** and **18**, Fig. 4).[24] Both compounds exhibited very wide temperature range smectic A phases (**17**: $T_g$: 48 °C; SmA → I: 189 °C; **18**: $T_g$: 63 °C; SmA → I: 262 °C). The tubular pillar[5]arene scaffold provides sufficient free volume for the azobenzene moieties to achieve reversible *cis-trans* photoisomerization within the mesophase. Moreover, their thin-films have shown light-triggered modulation of surface free energy and wettability.

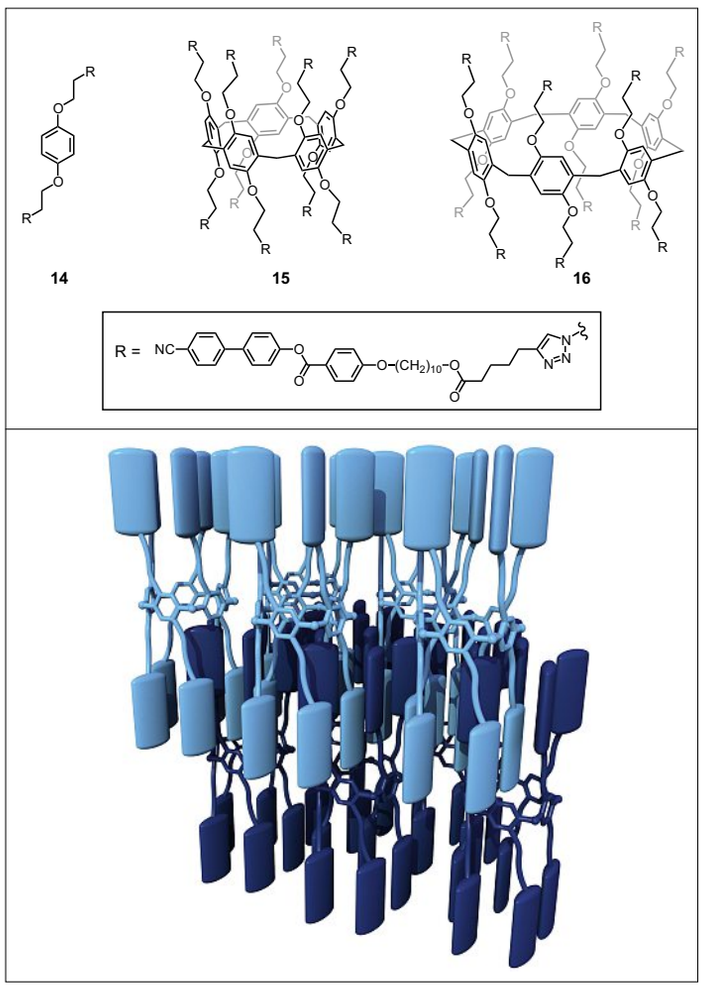



Fig. 3. Liquid-crystalline pillar[*n*]arene derivatives **15** and **16** and the corresponding monomeric model compound **14**. Bottom: postulated arrangement in the SmA phase for pillar[5]arene derivative **15** deduced from the X-ray diffraction studies.

## 4. Pillar[5]arene-containing Rotaxanes

### 4.1 *Synthesis of Pillar[5]arene-containing [2]Rotaxanes*

The host–guest chemistry of pillar[*n*]arene has been intensively investigated.[8] Owing to the electron-rich nature of their constitutive aromatic subunits, pillar[5]arenes are supramolecular receptors for electron-accepting molecules such as viologen[7,25] and imidazolium cations.[26,27] In addition to charge-transfer interactions between the electron-rich cavity of pillar[5]arenes and electron-deficient guest molecules, C–H···π interactions are also important for the formation of inclusion complexes.[8] Indeed, simple alkyl-substituted guests are effectively encapsulated in the cavity of pillar[5]arene derivatives to generate inclusion complexes.[16b,28] Such host–guest complexes are appropriate building blocks for the preparation of [2]rotaxanes. Stoddart and co-workers were the first to describe the synthesis of a pillar[5]arene-containing [2]rotaxane by reaction of a 1,8-diaminooctane guest with 3,5-di-*tert*-butylbenzaldehyde (Scheme 6).[29] The yield was however quite low owing to the low binding constant between the diamine guest and the pillar[5]arene host under the conditions used for

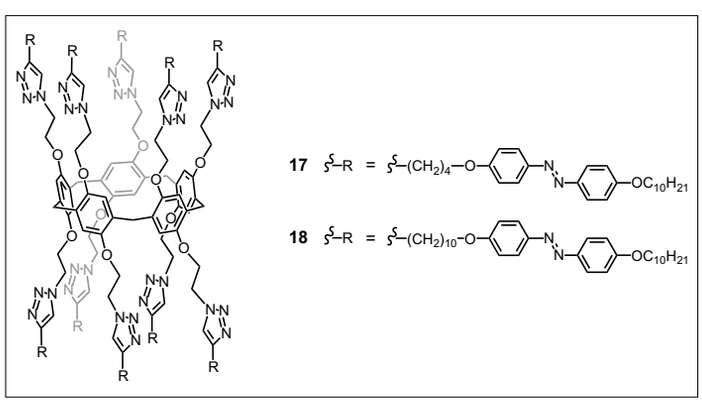
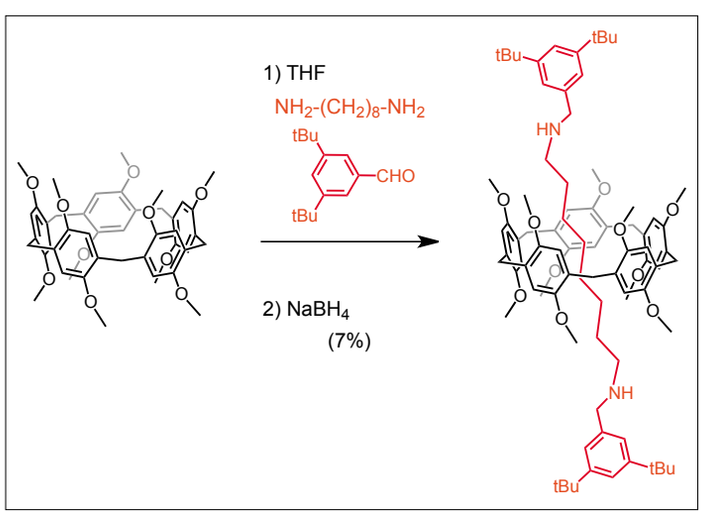


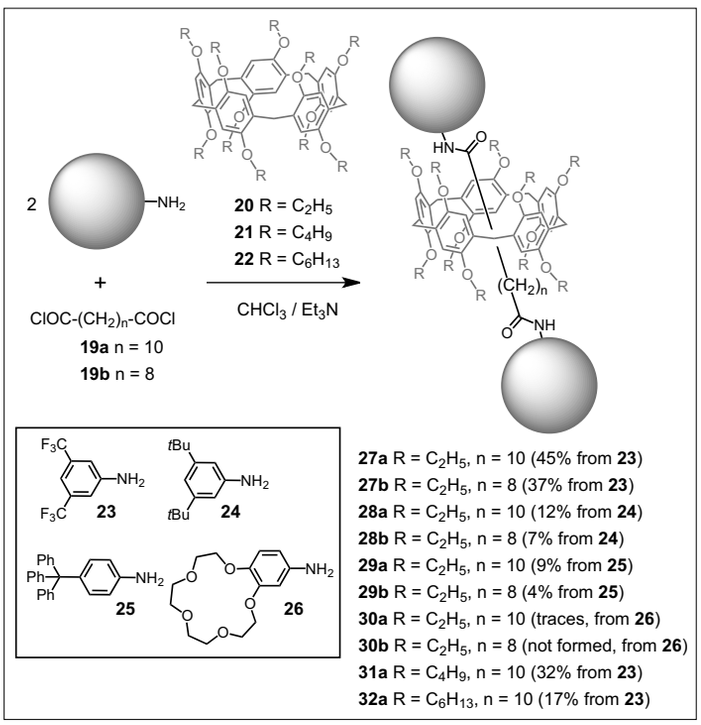

Fig. 4. Liquid-crystalline pillar[*n*]arene derivatives **17** and **18**.




Scheme 6. Preparation of the first pillar[5]arene-containing [2]rotaxane.

the condensation reaction. Following this first example, other [2]rotaxanes have been reported through the installation of bulky stoppers using different reaction conditions. Examples include reactions of acyl chlorides with alcohols[30] and copper-catalyzed alkyne-azide cycloadditions.[31] In the latter cases, the [2]rotaxanes were obtained in reasonably good yields.

Our two groups have recently shown that the reaction of diacyl chloride reagents with various amine stoppers is perfectly suited for the preparation pillar[5]arene-based [2]rotaxanes (Scheme 7).[32] The reaction conditions (solvent, stoichiometry) have been optimized to favor the formation of [2]rotaxanes. We also found that structural and electronic factors play an important role. In particular, the nature of the starting amine reagent has a dramatic influence on the yields of [2]rotaxanes. Therefore, the outcome of the reaction is not simply related to the association constant of the diacyl chloride reagent with the pillar[5]arene. Indeed, the difference in yields must be related to the difference in affinity for the various mono-acylated intermediates. The yields of [2]rotaxane are also influenced by steric factors. Effectively, significant differences have been observed when changing the size of the peripheral substituents of the pillar[5]arene building block or the chain length of the bis-acyl chloride reagent.




Scheme 7. Typical examples of pillar[5]arene-based [2]rotaxanes obtained from the reaction of diacyl chloride reagents with various amine stoppers.

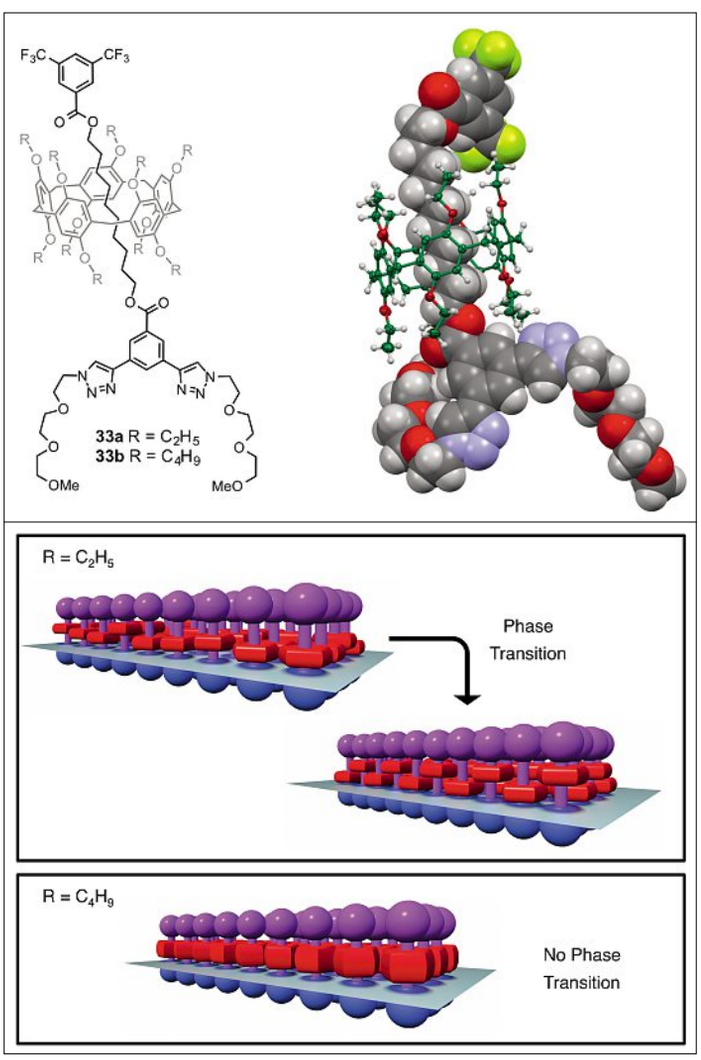



Fig. 5. Top left: amphiphilic pillar[5]arene-containing [2]rotaxanes **33a** and **33b** that have been used for the preparation of Langmuir films. Top right: X-ray crystal structure of **33a** (N: blue, O: red, F: pale green, C: gray for the dumbbell and dark green for the pillar[5]arene subunit). Bottom: schematic model of the Langmuir films obtained from **33a** and **33b**.

### 4.2 *Langmuir Films from Amphiphilic Pillar[5]arene-containing [2]Rotaxanes*

Whereas the synthesis of pillar[5]arene-containing rotaxanes has been at the center of this research, the most recent studies are concerned with their applications.[33] As part of this research, a good understanding of the self-organization capabilities of pillar[*n*]arene-containing rotaxanes is important for many future applications and our group has recently reported the organization of pillar[5]arene-containing [2]rotaxanes in Langmuir films.[34] The amphiphilic compounds are depicted in Fig. 5. In the particular case of the [2]rotaxane incorporating a 1,4-diethoxypillar[5]arene subunit, X-ray crystal structure analysis confirmed the structure of the compound.

Owing to an appropriate hydrophilic/hydrophobic balance, stable Langmuir films have been obtained for rotaxanes **33a** and **33b**. In the particular case of **33a**, one can note an increase of the compressibility of the film. The latter observation indicates the occurrence of some transition or molecular re-arrangement. In contrast, such a behavior was not evidenced for compound **33b**. The final molecular areas, extrapolated to zero surface pressure were 178±3 Å$^2$ for **33a** and 204±3 Å$^2$ for **33b**. Based on the observation of a phase transition for only one compound as well as the difference in molecular area, the molecular organizations within the Langmuir films obtained from **33a** and **33b** must be different. This was also confirmed by a different behavior upon compression/expansion cycles for the films obtained from the two rotaxanes. Effectively, a good reversibility is only

observed for compound **33a**. In contrast, no reversibility was observed for the corresponding butyl-substituted derivative (**33b**) most probably as a result of π–π interactions between neighboring pillar[5] arene moieties. In the case of **33a**, such intermolecular π–π interactions appear to be limited. We believe that the observed phase transition in the isotherm of **33a** is actually related to molecular rearrangement through gliding motions allowing the formation of a more compact film. In this way, π–π interactions between neighboring pillar[5]arene subunits are limited.

## 5. Conclusions

Pillar[*n*]arenes are a new class of macrocycles that are efficiently prepared from readily available building blocks. They have been already used for the construction of various multifunctional nanomolecules or supramolecular assemblies including [2]rotaxanes. Such compounds found applications in biology as multivalent ligands for specific lectines or as polycationic compounds for gene delivery. In materials science oriented research, the first examples of liquid crystalline pillar[5]arene have been reported. On the other hand, the ordering of pillar[5]arene derivatives has been also achieved at the air-water interface. The combination of pillar[*n*]arene chemistry with materials science or biology is actually appealing as the unique structural features of pillar[*n*]arenes (multivalency, shape and chirality) afford new materials that may be not produced by using other macrocyclic hosts. This chemistry is however still at an early stage of development and new applications can be expected in the near future.

Received: August 14, 2015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