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Insights into the synthesis of pillar[5]arene and its conversion into pillar[6]arene†

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The synthesis of pillar[5]arenes from *p*-dialkoxybenzene and formaldehyde in the presence of iron(III) chloride and tetramethylammonium chloride under mild reaction conditions was investigated in detail. For the first time, the presence of linear intermediate oligomers and their conversion into pillar[6]arenes was demonstrated. Incorporation experiments were carried out using methoxy- and ethoxy-functionalized pillar[5]arenes that were reacted respectively with 1,4-diethoxy- and 1,4-dimethoxybenzene, observing the formation of the corresponding co-pillar[6]arene derivatives, **PMe[5]Et[1]** and **PEt[5]Me[1]**. An experiment in which methoxy- and ethoxy-functionalized pillar[5]arenes were reacted together led to the major formation of scrambled **P[5]** derivatives characterized by a bell shape distribution of ethoxy and methoxy aromatic units. Co-Pillar[6]arenes **P[6]** were also detected by ESI-MS in minor amounts with a similar symmetrical distribution of substituents that allowed the proposal of multiple cleavage events occurring on the same macrocyclic ring forming in solution a series of smaller fragments, whose recombination leads to the observed product distribution of **P[5]** and **P[6]** derivatives.

Introduction

In supramolecular chemistry, macrocyclic compounds are usually exploited as hosts for specific guest targets to develop sensing systems,[1] catalysts,[2] or self-assembling[3] and self-healing materials.[4] The most renowned classes of hosts include cyclodextrins,[5] crown ethers,[6] calix[*n*]arenes[7] and cucurbit[*n*]urils[8] to name a few. In 2008, Ogoshi introduced pillar[*n*]arenes,[9] a new class of aromatic macrocycles prepared from simple and inexpensive aromatic starting materials. These macrocycles are characterized by a cylindrical semi-rigid shape with planar chirality, forming a highly electron-rich aromatic cavity with a diameter of 5.1 Å for pillar[5]arene (**P[5]**)[10] and 7.5 Å for pillar[6]arene (**P[6]**).[11] These cylindrical hosts can be decorated with flexible side chains that can be modified to improve solubility in organic or aqueous media. Pillararenes are nowadays exploited for their unique recognition properties towards neutral polarized guests[11,12] and they have been implemented in the preparation of several nanoscale systems ranging from rotaxanes[13] through vesicles,[14] supramolecular polymers[15] and adaptive crystals.[16] Because of their unique features, pillararenes have been employed in different fields like biosensing,[17] extraction of metal ions especially for f-block elements,[18] formation of vesicles for drug delivery,[19] small-molecule recognition,[20] and stimuli-responsive supramolecular polymers[21] to name a few.

Like calix[*n*]arenes and cucurbit[*n*]urils, the synthesis of pillar[*n*]arenes is particularly selective for one of the members of the family of the macrocyclic oligomers.[22] In fact, Ogoshi and co-workers initially obtained a symmetric **P[5]**[9] in 22% yield from 1,4-dimethoxybenzene with paraformaldehyde in the presence of $BF_3{\cdot}OEt_2$ as the Lewis acid catalyst in 1,2-dichloroethane. The synthesis was further improved, leading to **P[5]** being obtained in 71% yield using three equivalents of paraformaldehyde and the reduction of the reaction time to three minutes.[23] Interest towards this new class of host molecules spurred other groups to propose alternative synthetic methodologies based on the cyclization of similar aromatic derivatives in the presence of different Lewis acids such as $FeCl_3$, $AlCl_3$, $TiCl_4$, and $SnCl_4$ in various chlorinated solvents, but still under strictly anhydrous reaction conditions.[24] Szumna and Boinsky further proposed a moisture insensitive method making use of trifluoroacetic acid as the catalyst leading to the formation of **P[5]** in 81% yield.[25]

Different from **P[5]**, **P[6]** has been considered for some time as a secondary product of the reaction until Meier and co-workers, using chlorinated dry solvents and $FeCl_3$ as a catalyst, synthesized a mixture of pillar[*n*]arenes enriched in **P[6]**.[26] Mimicking the experimental conditions of Meier, the most recent procedures aimed at improving the amount of **P[6]**

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employing acid catalysts in stoichiometric and sub-stoichiometric amounts.[22,23] Similar to what is known for several other classes of host macrocycles, pillararenes can also be obtained through templated synthesis. Ogoshi described a procedure involving chlorocyclohexane as a templating solvent to obtain a methyl cyclohexyl substituted **P[6]** in 87% yield.[27] We recently demonstrated that the synthesis of pillararenes from *p*-dialkoxybenzene derivatives can be directed towards the **P[6]** macrocycle using small guest molecules as templates.[28] Very recently, a new simple, efficient and scalable method for the selective synthesis of **P[6]** derivatives has been developed by Zyryanov under solvent-free conditions using sulfuric acid as the catalyst.[29]

Even larger pillararenes are known: Meier's group published the synthesis of pillar[7]arenes from a $FeCl_3$-catalyzed condensation reaction of 1,4-dimethoxybenzene with paraformaldehyde in chloroform or, alternatively, from the *p*-toluenesulfonic acid-catalyzed condensation reaction of 2,5-bis(benzyloxymethyl)-1,4-dimethoxybenzene.[30] Pillar[8–10]arenes were synthesized in less than 2% yield by Hou and collaborators using chloroform as a non-templating solvent starting from 1,4-diethoxybenzene as a monomer at room temperature.[31] Nevertheless, the purification of pillar[8–10]arenes was compromised by the formation of soluble linear oligomers. The latter were avoided in the high temperature methodology adopted by Ogoshi that used **P[5]** as the starting material.[32]

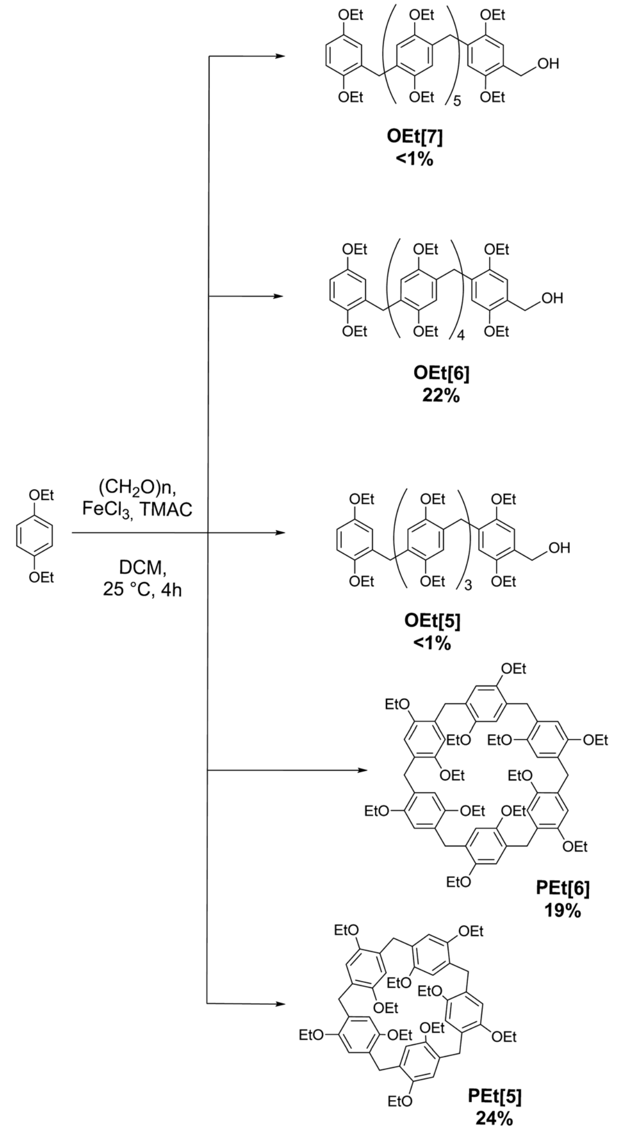
The equilibrium reaction between different pillararene homologues in the cyclization process was then studied by Nierengarten[33] who demonstrated the synthesis of **P[5]** and its analogues to be driven by dynamic covalent bond formation under Friedel–Crafts conditions. It was shown that **P[5]** is the thermodynamic product while **P[6]** is the kinetic one when the condensation reaction is carried out starting from 2,5-bis(bromomethyl)-1,4-dialkoxybenzenes. Directing the synthesis toward larger members of the family is still a challenging area of research and Ogoshi and co-workers proved that the equilibrium can be shifted from **P[5]** to **P[6]** by switching the solvent from 1,2-dichloroethane to chlorocyclohexane,[27] and *vice versa*. In this context, even hybrid macrocycles were successfully synthesized in quite high yields under thermodynamic control.[34] Albeit a large body of work has been carried out in the synthesis of pillararenes, further effort is needed to understand the mechanism of the macrocyclization as well as the interconversion between the most common **P[5]** and **P[6]** derivatives. Here, we report evidence for the formation of oligomeric intermediates in the synthesis of these macrocycles starting from *p*-dialkoxybenzene derivatives and formaldehyde in the presence of $FeCl_3$ and tetramethylammonium chloride[28] (TMAC) and their conversion into **P[6]**. Further investigations on the interconversion between **P[5]** and **P[6]** using an integrated approach based on the monitoring of the reaction mixture through NMR and ESI-MS analysis are described.

Results and discussion

The cyclization reaction

Recently, we reported a new cation-templated synthesis of the larger 1,4-diethoxypillar[6]arene (**PEt[6]**) that was isolated in 44% yield.[28] We observed that the ratio between **PEt[6]** and 1,4-diethoxypillar[5]arene (**PEt[5]**) was changing as a function of the duration of the quenching process with water. In order to confirm this behavior, we considered a procedure based on the use of 1,4-diethoxybenzene, formaldehyde, $FeCl_3$, and TMAC in dichloromethane (DCM) at room temperature (Scheme 1) and focused our attention on the workup procedure. We observed that the initial product distribution after quenching with water followed by product isolation was 24% **PEt[5]** and 19% **PEt[6]**.

This distribution drastically changed when the water–quenching mixture was maintained under vigorous stirring for one week, obtaining 16% **PEt[5]** and 44% **PEt[6]**. The modification of the product distribution is evident also from the ^1H



Scheme 1 Synthesis of **PEt[*n*]** (*n* = 5, 6) by the reaction of 1,4-diethoxybenzene with formaldehyde in DCM, in the presence of TMAC and $FeCl_3$. After a rapid quenching of the reaction with water, some linear oligomers **OEt[*n*]** (*n* = 5, 6, 7) as reaction by-products were observed.

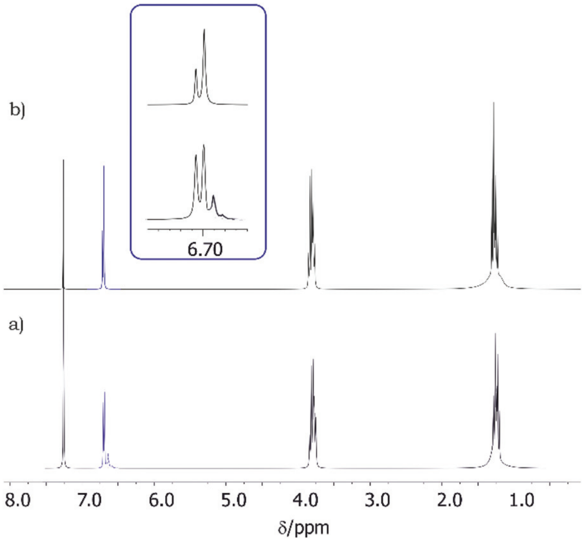


Fig. 1 ^{1}H NMR spectra of the cyclization reaction of 1,4-diethoxybenzene with formaldehyde in the presence of TMAC as a template and FeCl$_3$ as a catalyst in DCM at room temperature for 4 h, (a) right after quenching with water and (b) quenched stirring with water for one week before isolation.

NMR spectra shown in Fig. 1 where the ratio between the aromatic peak of **PEt[6]** (6.70 ppm, 12 H) increased with respect to the aromatic peak of **PEt[5]** (6.72 ppm, 10 H). A third small and broad signal close to the previous two was present in the ^{1}H NMR spectra of the reaction mixture before workup (Fig. 1a), which disappeared after stirring the mixture for one week in the quenching step (Fig. 1b). This is clearly indicative of an ongoing equilibration involving two macrocyclic species and other minor products present in the crude final reaction mixture (Scheme 1).

In order to better elucidate the structure of such intermediate species, we isolated through column chromatography the major component of this fraction in 22% yield and assigned its structure by EI-MS and NMR (see the ESI†) as the oligomeric benzylic alcohol **OEt[6]**. Other minor oligomers were detected such as the benzyl alcohols **OEt[5]** and **OEt[7]**, whose amount was very low (<1%) (Scheme 1). The relative amounts of these secondary oligomers were determined by comparing the intensity of the peaks in the EI-MS spectrum. Due to their minor relative abundance, from now on, only the linear hexameric oligomer **OEt[6]** will be considered.

Oligomer OEt[6] conversion into PEt[6]

The mixture of oligomers mainly composed of **OEt[6]** was used as a starting material to investigate by MS spectroscopy its conversion into the target pillararene products. **OEt[6]** was combined with paraformaldehyde, FeCl$_3$ and TMAC in dichloromethane and water and the reaction mixture was stirred for four days observing the formation of **PEt[6]** in 56% isolated yield. ESI-MS analysis confirmed unambiguously this result observing the peaks attributed to **PEt[6]@NH$_4^+$** at m/z 1086.64, **PEt[6]@Na$^+$** at m/z 1091.59 and **PEt[6]@K$^+$** at m/z 1107.57, while the peaks at m/z 891.51, 908.53, 913.49, and 929.47, ascribable to the analogue **PEt[5]** complexes were not detected (see the ESI†). To better understand the species actively involved in the reaction, all the combinations of **OEt[6]** with the other reagents and promoters were investigated (Table 1). As expected, the methylene source (paraformaldehyde) was superfluous to complete the reaction (Table 1, entry 1), since **OEt[6]** contains the benzylic moiety sufficient for the ring-closure to **PEt[6]**. In contrast, the reaction was strongly dependent on the presence of both TMAC and FeCl$_3$. In particular, the templating species TMAC rather than the metal catalyst showed a slightly greater influence on **PEt[6]** yields. In fact, the macrocycle was formed in 55% yield in the presence of both TMAC and FeCl$_3$ (Table 1, entry 2). Conversely, in the presence of only FeCl$_3$ or TMAC (Table 1, entries 3 and 4) **PEt[6]** was obtained in 25% and 32% isolated yield, respectively.

Table 1 Synthesis of **PEt[6]** from **OEt[6]** in DCM at 25 °C, in the presence (+) or absence (–) of paraformaldehyde, FeCl$_3$ and TMAC

#	(HCHO)$_n$	FeCl$_3$	TMAC	Isolated yield (%)
1	+	+	+	55
2	–	+	+	55
3	–	+	–	24
4	–	–	+	32

These results can be explained considering that the benzyl alcohol moiety present in the oligomer **OEt[6]** can easily lose water in the presence of FeCl$_3$ as a Lewis acid as well as in the presence of the templating TMAC forming the corresponding benzyl cation that leads to ring closing forming the desired product **PEt[6]**. These unprecedented observations on the formation and conversion of the oligomers extend their role from undesired by-products to valuable intermediates in the synthesis of **PEt[6]** and prove the spontaneous tendency of the linear oligomers **OEt[6]** to convert into **PEt[6]** under the described reaction conditions.

Conversion of PEt[5] into PEt[6]

The amount of **PEt[6]** obtained through the conversion of the linear oligomers was not sufficient to fully justify the yield increase of the hexameric pillararene obtained on prolonging the quenching procedure. Therefore, our attention was further focused on the possible conversion of **PEt[5]** into **PEt[6]**. Similar reactions were already described by Ogoshi and coworkers[22,27] to occur at 50 °C starting from **PEt[5]** in chloroform for 1 h in the presence of BF$_3$·OEt$_2$, or from the corresponding cyclohexyl substituted **P[5]** transformed into the corresponding **P[6]** derivative in chlorocyclohexane in the presence of BF$_3$·OEt$_2$. It is worth noting that in both cases the presence of a Lewis acid was mandatory to favor the ring opening of **PEt[5]**.

We performed the reaction under the same experimental conditions studied for the conversion of the oligomers by mixing **PEt[5]** with paraformaldehyde in the presence of $FeCl_3$ and TMAC in DCM/H_2O at 25 °C. A series of control experiments were carried out in order to determine the single factors affecting the conversion of **PEt[5]** into **PEt[6]**, analyzing the reaction mixtures by ESI-MS and in some cases isolating **PEt[6]**. The formation of **PEt[6]** (8% yield) was observed when the reaction mixture was maintained under vigorous stirring as evidenced by the ESI-MS spectra (Fig. 2) of the reaction mixtures after one and four days of quenching, in which complexes with typical background ions like NH_4^+, Na^+ and K^+ are observed. Also, the tetramethylammonium (TAM^+) complex of **PEt[5]** was observed at 964.59 *m*/*z* (Fig. 2).

In the spectrum of Fig. 2a, the sum of the intensities of all **PEt[6]** peaks was only 1% compared to that of all the **PEt[5]** peaks, clearly showing that the conversion of the smaller into the larger macrocycle takes place very slowly. After four days, the equilibrium was reached observing 10% of **PEt[5]** that was converted into **PEt[6]** as determined by the ratio of the intensities of all peaks, further confirmed by the 8% isolated yield of **PEt[6]** after preparative TLC.

The reaction was repeated without paraformaldehyde, leading to the formation of **PEt[6]** in nearly identical isolated yield (8%). This experiment showed that a reactive methylene source was not necessary for the conversion of **PEt[5]** into **PEt[6]**. Based on this observation, all the subsequent experiments were carried out in the absence of paraformaldehyde. Most interestingly, the removal of TMAC or $FeCl_3$ drastically affected the reaction, leading to negligible formation of **PEt[6]**. All these results confirm that, similarly to the ring-closing reaction from **OEt[6]** to **PEt[6]**, the conversion of **PEt[5]** into **PEt[6]** occurs in a few days, in the presence of $FeCl_3$ to promote the ring opening with TMAC acting as a probable templating effect.

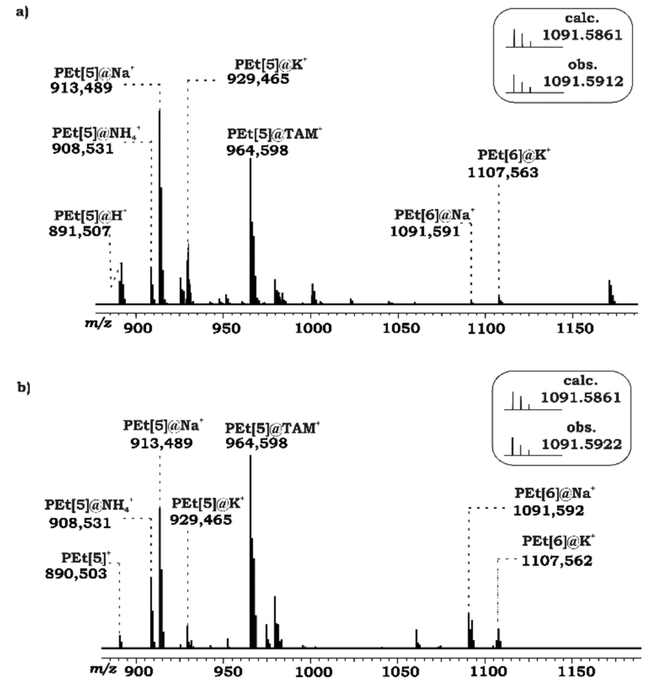


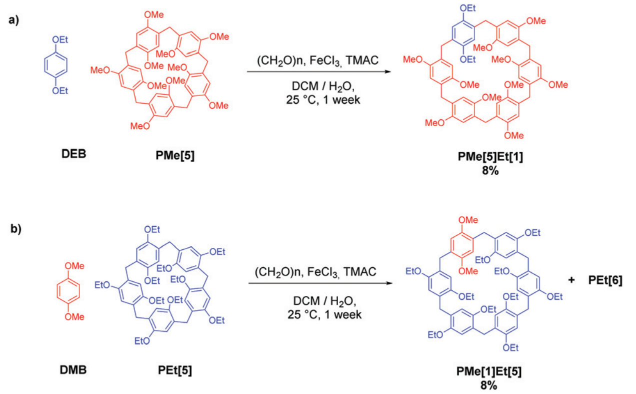
Fig. 2 ESI-FTICR-MS spectra of **PEt[5]** conversion into **PEt[6]** in the presence of paraformaldehyde, $FeCl_3$ and TMAC, (a) after one day, (b) after four days of quenching with water. In both spectra are reported the calculated and experimental isotopic distribution for the complex **PEt[6]@Na$^+$**.

The role of the Fe(III) catalyst in the reaction was further investigated considering that $FeCl_3$ in water contributes to the increase of the Brønsted acidity of the aqueous phase.[35] To investigate this, we performed the reaction with **PEt[5]** in the presence of 1×10^{-3} M HCl without $FeCl_3$ observing no conversion into **PEt[6]**. This evidence suggested that the conversion of **PEt[5]** into **PEt[6]** was promoted more likely from an interaction between the oxygen atoms of **PEt[5]** and Fe(III) as a Lewis acid rather than being promoted by the induced Brønsted acidity.

The reverse reaction from **PEt[6]** to **PEt[5]** was also studied to have a better clue on the conversion between the two macrocycles. Starting from **PEt[6]** in the presence of all the reactants, the cyclic pentamer was not observed, highlighting once again the higher thermodynamic stability of **PEt[6]**. Under our experimental conditions, the conversion of **PEt[6]** into **PEt[5]** was not observed probably due to the presence of TMAC as a template for **PEt[6]**.

Incorporation experiments for the synthesis of co-pillar[6]arenes

To demonstrate the equilibrium between the macrocyclic and open forms of pillar[5]arenes, a series of experiments were carried out under the same experimental conditions in the presence of labelled monomers. When in the presence of $FeCl_3$, TMAC and paraformaldehyde, **PMe[5]** was reacted with 1,4-diethoxybenzene (**DEB**) or **PEt[5]** was reacted with 1,4-dimethoxybenzene (**DMB**), co-pillar[6]arene **PMe[5]Et[1]** (Scheme 2a) and **PMe[1]Et[5]** (Scheme 2b) were formed, respectively. In addition, small amounts of **PEt[6]** were observed in the second experiment (Scheme 2b), in agreement with the **PEt[5]** to **PEt[6]** conversion discussed above. The ESI mass spectra of purified **PMe[1]Et[5]** and **PMe[5]Et[1]** are reported in Fig. 3a and b, respectively.



Scheme 2 Incorporation experiment between (a) DEB and **PMe[5]** and (b) DMB and **PEt[5]**.

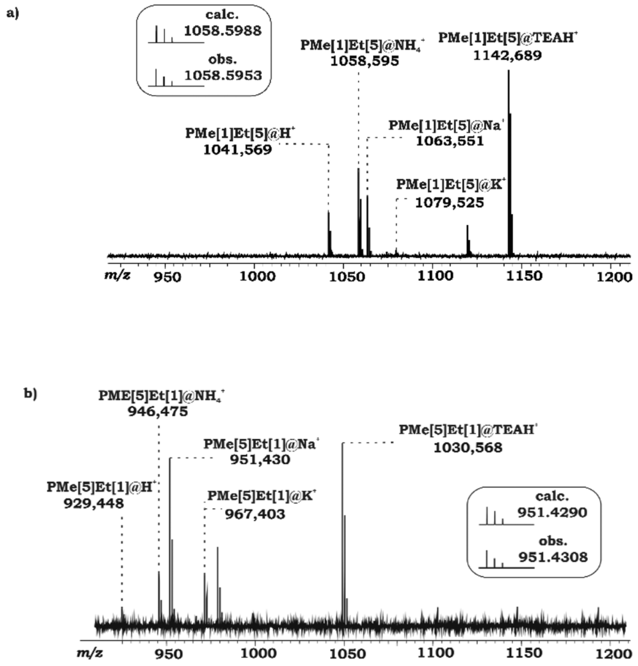
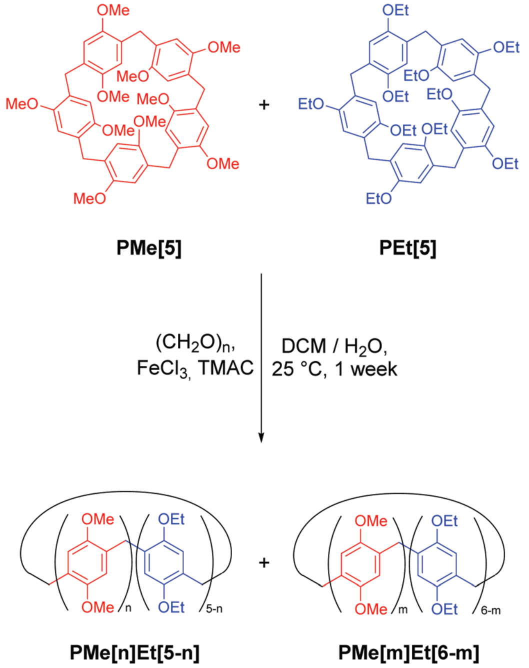


Fig. 3 (a) FTICR-MS spectrum of **PMe[1]Et[5]** and compared isotopic distribution for the complex **PMe[5]Et[1]@Na$^+$**; (b) FTICR-MS spectrum of **PMe[5]Et[1]** and comparison of the calculated and experimental isotopic distribution for the complex **PMe[1]Et[5]@NH$_4^+$**.



Scheme 3 Scrambling experiment between **PMe[5]** and **PEt[5]** resulting in **PMe[*n*]Et[5-*n*]** and **PMe[*m*]Et[6-*m*]** where $n = 0–5$ $m = 0–6$.

These incorporation experiments confirmed the hypothesis of an equilibrium between cyclic and open forms of **P[5]**, which arises from the cleavage of a methylene bridging unit. The latter, in the form of a benzyl cation, reacts with the free 1,4-dialkoxybenzene elongating the open chain that can eventually close to **P[6]** in the presence of a suitable methylene source from paraformaldehyde aided by the presence of TMAC.

These insertion experiments suggest possible shortcut synthetic approaches for the synthesis of co-pillar[6]arenes bearing just one different aromatic unit that are alternatives to the most commonly used strategy comprising double alkoxy deprotection from the same aromatic unit of the macrocycle using BBr_3 under strict conditions and further alkylation with the desired units.[36]

Scrambling experiment between two differently substituted P[5]s

To shed light on the possible conversion mechanism between the smaller and the larger pillararenes, we designed a scrambling experiment between two different substituted **P[5]**, **PMe[5]** and **PEt[5]** respectively (Scheme 3). The reaction was performed in the presence of $FeCl_3$ and TMAC in dichloromethane and water at 25 °C and the product distribution was characterized by ESI-QTOF-MS after one-week of quenching reaction (Fig. 4). The peak assignment and the corresponding relative abundance present in the reaction mixture are reported in Table S2 in the ESI.†

We observed two different product distributions that are directly ascribable, one to the series of co-pillar[5]arenes (Fig. 4a and Table S2† entries 1–12) and the other to the series of co-pillar[6]arenes (Fig. 4b and Table S2† entries 13–22). Focusing on the first distribution, we observed the formation of all the scrambled species bearing different numbers of methoxy and ethoxy substituents existing in between **PMe[5]** and **PEt[5]**. As clearly visible from Fig. 4a, the distribution shows a profile where the original reagents **PMe[5]** and **PEt[5]** were highly converted into the co-pillar[5]arene species. The two most abundant co-pillar[5]arenes were **PMe[3]Et[2]** and **PMe[2]Et[3]** for which the position of the two identical units is not to be intended to be contiguous. The symmetrical distribution is also indicative of a similar easy ring opening for the two reagents **PMe[5]** and **PEt[5]**.

The scrambling reaction also produced a modest amount of pillar[6]arenes (Fig. 4b), in agreement with what has been described above for the ring-expansion of **PEt[5]** in the presence of $FeCl_3$ and TMAC. In this case the distribution showed again a certain level of symmetry, in particular **PMe[6]** was hardly detected and **PEt[6]** was rather weak and conversely the intermediate co-pillar[6]arenes **PMe[2]Et[4]**, **PMe[3]Et[3]** and **PMe[2]Et[4]** were the most abundant species detected, also in this case with the position of identical units not to be intended to be contiguous.

To better rationalize the results, for each pillararene containing different alkoxy substituents we summed the intensities of the MS peaks regardless of the bound ion species (proton or ammonium, see the ESI†). In this way it was possible to better compare the relative amounts of the different scrambling **P[5]** and **P[6]** products. This analysis is reported in Fig. 5 from which the bell-shape distribution can be appreciated for both macrocycles. The product distribution for the **P[5]** products clearly speaks for an equilibrium between the cyclic structures and not only the **O[5]** corresponding open derivative, but also a series of smaller dimeric, trimeric or even monomeric benzyl alcohol units derived by multiple cleavage reactions on the original macrocycle. In fact, the observed highly symmetrical distribution of **P[5]** as well as **P[6]** derivatives is the same as the one that can be expected theoretically starting from **DMB** and **DEB** with formaldehyde, excluding any steric or electronic cross-effects between the aromatic reagents.

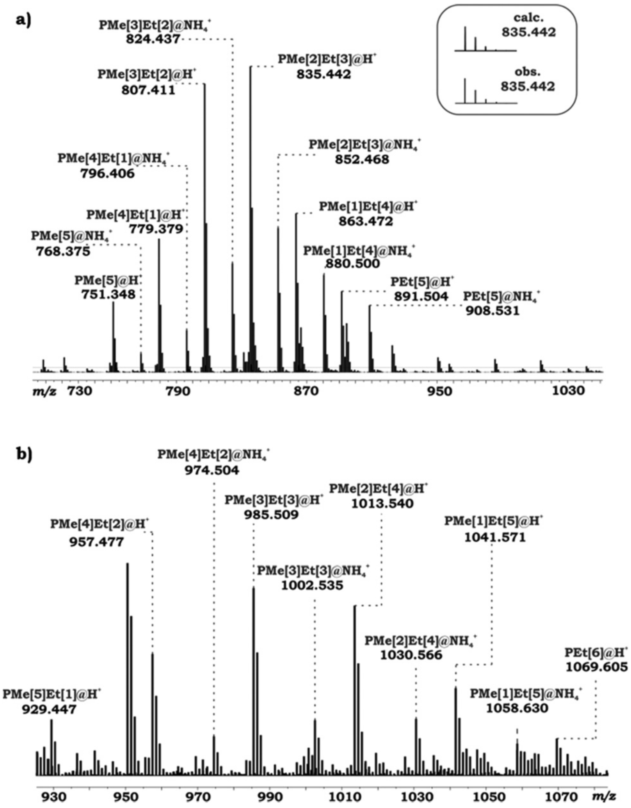


Fig. 4 (a) ESI-QTOF-MS spectrum of the reaction mixture **PMe[5]–PEt[5]** zoomed between 700 and 1030 *m/z* and compared isotopic distribution for the complex **PMe[2]Et[3]@H$^+$**; (b) ESI-QTOF-MS spectrum of the reaction mixture **PMe[5]–PEt[5]** zoomed between 900 and 1100 *m/z*.

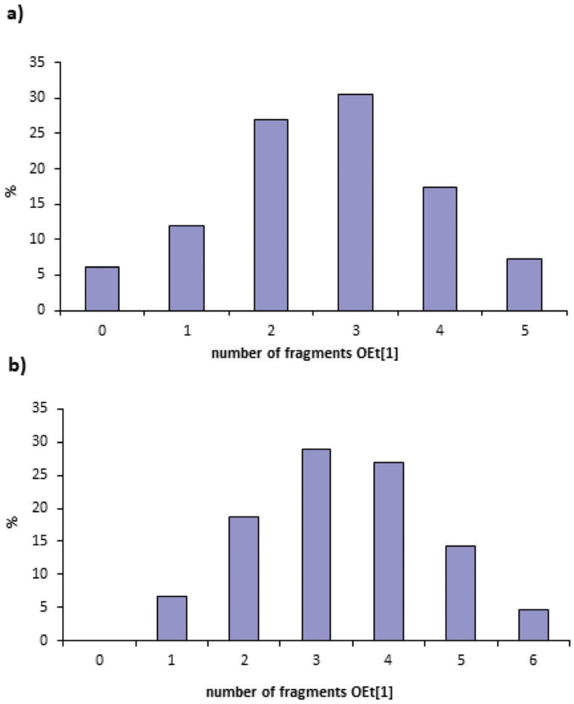


Fig. 5 (a) Normalized relative abundance of the fragments for the **P[5]** scrambling products; (b) normalized relative abundance of the fragments for the **P[6]** scrambling products.

Conclusions

In conclusion, herein we demonstrated that in the synthesis of pillararenes catalyzed by $FeCl_3$ and templated by **TMAC**, a change in the pillararene product distribution occurs as a function of the quenching procedure. This phenomenon could be ascribable to both (i) the conversion of **PEt[5]** into **PEt[6]** and (ii) the ring closure of some oligomeric linear benzylic alcohol by-products that for the first time have been isolated and characterized. The more abundant among these oligomers could further react to give **PEt[6]** in 55% yield in the presence of $FeCl_3$ and a template.

Under the same reaction conditions, we demonstrated the conversion of **PEt[5]** into **PEt[6]** in higher yield (8% yield) compared to the conversions previously reported by Ogoshi and coworkers.[27] Exploiting the ring opening reaction of pillararenes, we proved the synthesis of co-pillararenes **P[6]** with one single different aromatic unit reacting **PMe[5]** and **PEt[5]** with **DEB** and **DMB**, respectively.

Further support for the interconversion between pillararenes was provided by investigating the scrambling experiment between **PMe[5]** and **PEt[5]**. The observed product distributions indicated that under the reported experimental conditions the cyclic structures were subjected to an equilibrium with only the **O[5]** corresponding open oligomers. This implies that multiple cleavage events occur on the same macrocyclic ring forming in solution a series of smaller fragments that can recombine leading more favourably to **P[5]** derivatives as well as minor amounts of **P[6]** derivatives. In both cases the formed pillararenes showed a symmetrical distribution of alkoxy substituents, as if the macrocycles were completely disassembled and further re-assembled. All this new experimental evidence on the synthesis and conversion between pillararenes represents a step forward in the understanding of the chemistry of this fascinating class of host systems. We hope it will help to spur the investigation of new synthetic methods, especially for the preparation of larger macrocycles bearing different aromatic units.

Conflicts of interest

There are no conflicts to declare.

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