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Syntheses of Copillar[5]arenes by Co-oligomerization of Different Monomers

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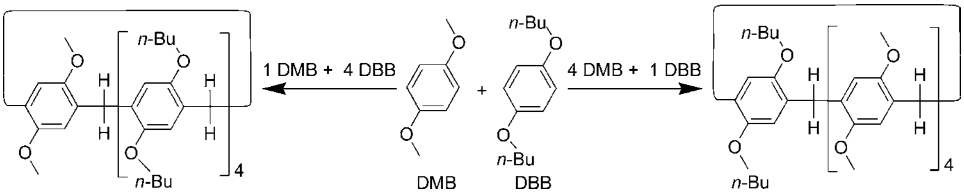
ABSTRACT



Three copillar[5]arenes, pillar[5]arenes containing different repeating units, were successfully prepared by co-oligomerization of different monomers. It was demonstrated that the yields of pillararenes could be improved by using hydroquinone diethers with appropriate aliphatic chain lengths. Pseudorotaxane-type threaded structures were obtained in the solid state by the inclusion of an *n*-hexane molecule into the cavity of either a homopillar[5]arene, a pillar[5]arene containing only one repeating unit, or a copillar[5]arene.

As the third generation of supramolecular hosts, calixarenes are described as macrocycles with (almost) unlimited possibilities.[1a] By functionalization of the upper or lower rim, they have been widely used in the recognition of ions and molecules and fabrication of supramolecular assemblies.[1] Recently, Ogoshi et al. reported a new type of calixarene analogue, pillar[5]arenes, prepared from 1,4-dimethoxybenzene catalyzed by $[BF_3{\cdot}O(C_2H_5)_2]$.[2a] Pillararenes have shown interesting properties in host−guest chemistry with electron-accepting molecules.[2] Later, Cao et al. synthesized pillar[6]arenes from 1,4-dialkoxy-2,5-bis(alkoxymethyl)benzene using *p*-toluenesulfonic acid as the catalyst.[3] Recently, polypseudorotaxanes were constructed with pillar[5]arenes as the cyclic rings and viologen polymers as the main chains.[4] Pillararenes reported up to now were all synthesized from homo-oligomerization of one monomer.[2−4] Their highly symmetrical structures make them difficult to selectively functionalize, greatly limiting their applications. The introduction of different repeating units into pillararenes makes it possible to control their physical properties, conformations, and host−guest binding, as demonstrated in calixarene,[1,5] cucurbituril,[6] and copolymer[7] chemistries. We are interested

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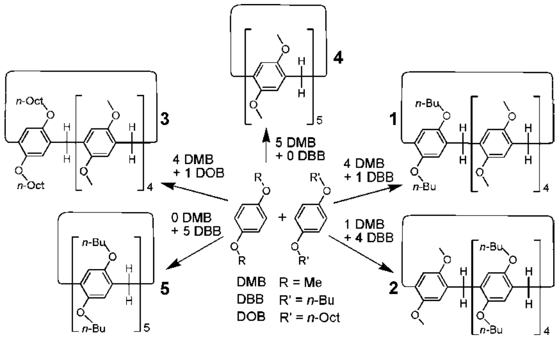
in the syntheses of copillararenes, which are pillararenes containing different repeating units.

There are at least two possible ways to make copillararenes: selective modification of homopillararenes, which are pillararenes containing only one repeating unit, or co-oligomerization of different monomers. At first we tried to selectively dealkylate dialkylhomopillar[5]arenes as done with calixarenes.[5b] This route proved to be unfeasible because there were so many possible products that were really difficult to separate. Therefore, we used the second way and successfully synthesized three copillar[5]arenes, **1**, **2**, and **3**, by co-oligomerization of different monomers (Scheme 1).

Scheme 1. Preparation of Pillar[5]arenes by Oligomerization of Hydroquinone Diethers



To make copillar[5]arene **1**, a mixture of 4 equiv of 1,4-dimethoxybenzene (DMB), 1 equiv of 1,4-dibutoxybenzene (DBB), 5 equiv of paraformaldehyde, and 5 equiv of [BF_3·$O(C_2H_5)_2$] was stirred in 1,2-dichloroethane under nitrogen atmosphere at room temperature for 4 h. After purification by column chromatography, copillar[5]arene **1** was isolated in 16% yield, lower than the 22% yield of homopillar[5]arene **4** from the oligomerization of DMB under the same reaction conditions.[2a] Pillararenes with other compositions could not be isolated, but peaks related to homopillar[5]arene **4** and the copillar[5]arene containing 3 DMB units and 2 DBB units were observed in the mass spectrum of the product mixture. When 1 equiv of DBB was replaced by 1 equiv of 1,4-di(octyloxy)benzene (DOB) in this reaction, copillar[5]arene **3** was obtained in 27% yield, showing that the yield of the target copillararene could be improved by using a hydroquinone diether comonomer with longer aliphatic chains. For further investigation, we reversed the ratio of the two comonomers; 1 equiv of DMB and 4 equiv of DBB were used. In this case, copillar[5]arene **2** containing 1 DMB unit and 4 DBB units was isolated in 9% yield while homopillar[5]arene **5** was obtained in 13% yield. Because of their structural similarity, separation of **2** and **5** was difficult. We had to use a very low-polarity eluent, 600:1 petroleum ether/ethyl acetate (v/v). In sharp contrast, homopillar[5]arene **5** was produced in 55% yield from the oligomerization of DBB. These experiments indicate that copillar[5]arenes can be prepared by co-oligomerization of different monomers, and the yields of pillar[5]arenes can be improved when hydroquinone diether monomers with appropriate aliphatic chain lengths are used.

Copillar[5]arenes **1** and **2** have better solubility in organic solvents such as *n*-hexane, chloroform, acetone, and acetonitrile than homopillar[5]arene **4**. The melting points of **1** (147.9 °C) and **2** (132.9 °C) are between those of homopillar[5]arenes **4** (248.8 °C) and **5** (131.2 °C). The UV−vis spectroscopy of pillar[5]arenes **1**−**5** in chloroform are almost the same, with a common peak at 295 nm due to the same annular aromatic part. Further investigations on these pillar[5]arenes were carried out with proton NMR (Figure 1). Since copillar[5]arenes **1** and **2** have different repeating units, signals of their aromatic protons H_1 split. By comparison of peak integration ratios of different protons, we can see that the portion of the DBB units increases (the green rectangle in Figure 1) while that of the DMB units decreases (the blue rectangle in Figure 1) in the following order: **4** → **1** → **2** → **5**, in accordance with their chemical structures. From the variable-temperature proton NMR spectra of **1** and **2**, the coalescence temperature (T_c) was estimated on the coalescence signal of the methylene protons (H_4) of them. The coalescence temperature of **2** is −15 °C, which is close to the T_c of **5**.[2e] However, the signals of H_4 on **1** were not split even at −45 °C, because it has four relatively smaller methyl groups on each side. As the number of smaller substituents at the upper and lower rims increases, the conformational freedom of copillar[5]arenes increases. Further investigation shows that the ratio of different repeating units of pillar[5]arenes can influence their host-gust binding. The complexation of **1** with *n*-octyltrimethyl ammonium hexafluorophosphate in chloroform is in rapid

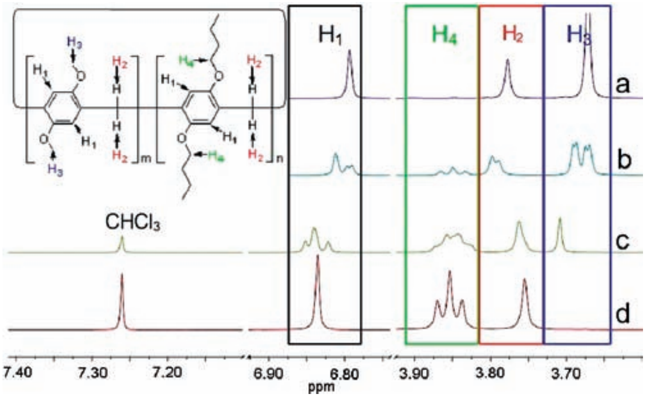


Figure 1. Partial ^1H NMR spectra (400 MHz, $CDCl_3$, 20 °C) of (a) homopillar[5]arene **4** ($m = 5$, $n = 0$); (b) copillar[5]arene **1** ($m = 4$, $n = 1$); (c) copillar[5]arene **2** ($m = 1$, $n = 4$); (d) homopillar[5]arene **5** ($m = 0$, $n = 5$).

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exchange on the proton NMR time scale, while the complexation of **5** and OTMA is a slow exchange system under the same conditions with a higher association constant.

Single crystal X-ray analyses (Figure 2) further confirmed the formation of copillar[5]arenes **1** and **3** and homopillar[5]arene **5**. Crystals of $\mathbf{1}\supset(CH_2Cl_2)_2$ were grown by slow evaporation of a solution of **1** in a dichloromethane/acetonitrile mixture, whereas single crystals of $\mathbf{3}\supset n\text{-}C_6H_{14}$ and $\mathbf{5}\supset n\text{-}C_6H_{14}$ were grown by slow evaporation of solutions of **3** and **5** in *n*-hexane and a mixture of petroleum ether and ethyl acetate (600:1 v/v), respectively. The crystal structure of copillar[5]arene **1** gave direct proof that it contains four DMB units and one DBB unit (Figure 2, a and d). Because of the rigid equilateral pentagon pillar structure, except for the DBB part, the crystal structure of copillar[5]arene **1** is almost the same as that of homopillar[5]arene **4**.[2a] The biggest difference between the crystal structures of **1** and **4** is that a disordered acetonitrile molecule was included in the cavity of **1**, while two dichloromethane molecules were included in the cavity of **4** here. The shortest distance between the chlorine atoms of the dichloromethane molecules and the aromatic carbon atoms on **1** is 3.30 Å, which is shorter than 3.45 Å, the sum of the van der Waals radii of carbon and chlorine atoms,[8] indicating the existence of halogen-π-type halogen bonds.[9] The H···π-plane distances of the four hydrogen atoms of the two dichloromethane molecules are 2.73 and 2.80 Å, shorter than 3.05 Å, implying the existence of C−H···π interactions.[10]

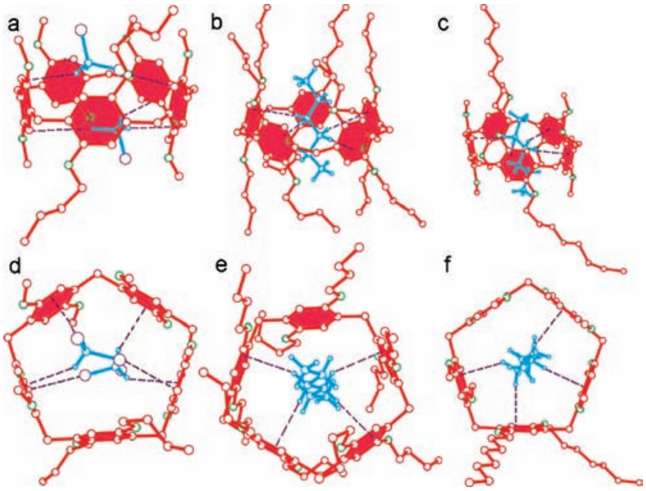

Figure 2. Views of the crystal structures of $\mathbf{1}\supset(CH_2Cl_2)_2$ (a, d), $\mathbf{5}\supset n\text{-}C_6H_{14}$ (b, e), and $\mathbf{3}\supset n\text{-}C_6H_{14}$ (c, f). Hydrogens on **1**, **3**, and **5** were omitted for clarity; **1**, **3**, and **5** are red, oxygen atoms are green, chlorine atoms are magenta, and dichloromethane and *n*-hexane molecules are blue. The purple dotted lines indicate C−H···π interactions and halogen bonds.

It is amazing that there is an *n*-hexane molecule symmetrically included in the cavity of homopillar[5]arene **5**, forming a pseudorotaxane in the solid state (Figure 2, b and e). This indicates that **5** may be able to act as a host for long-chain alkanes. There are four hydrogen atoms on the included *n*-hexane with H···π-plane distances, 2.84−3.00 Å, shorter than 3.05 Å too, so four C−H···π interactions are believed to exist between the included *n*-hexane and **5**. These are the main driving forces for the inclusion of the *n*-hexane molecule into the cavity of **5**. Although the C−H···π interaction is the weakest hydrogen bond, it is stronger than the van der Waals force.[11]

The chemical structure of copillar[5]arene **3** was also confirmed by its X-ray crystal structure (Figure 2, c and f). Again an *n*-hexane molecule was included into the cavity of **3** to form a pseudorotaxane driven by the C−H···π interactions.

In conclusion, three copillar[5]arenes were successfully made *via* co-oligomerization of different monomers. The yields of pillararenes can be improved by using hydroquinone diethers with appropriate aliphatic chain lengths. The introduction of different repeating units to prepare copillararenes provides a convenient way to the control of guest-binding and selective functionalization of pillararenes. The pseudorotaxane formation between homopillar[5]arene **5** and *n*-hexane in the solid state implies potential applications of pillararenes in the fabrication of functional interlocked structures.[12]

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Supporting Information Available: Synthetic procedures, characterizations, crystal data, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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