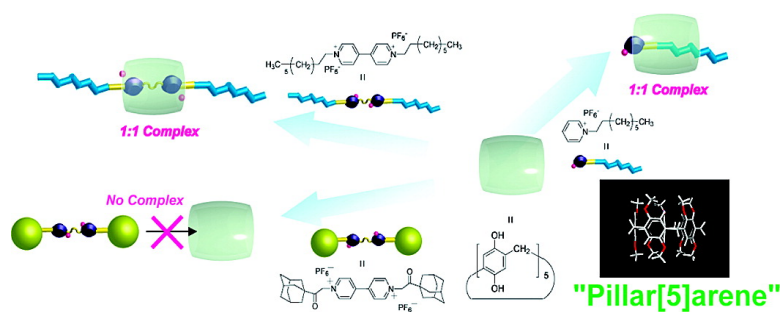


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## *para*-Bridged Symmetrical Pillar[5]arenes: Their Lewis Acid Catalyzed Synthesis and Host–Guest Property

Tomoki Ogoshi,\* Suguru Kanai, Shuhei Fujinami, Tada-aki Yamagishi, and Yoshiaki Nakamoto\*

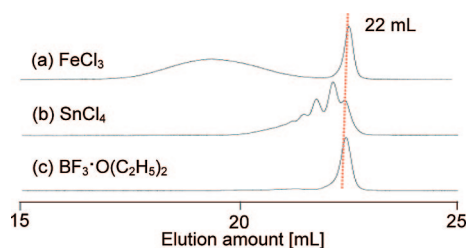
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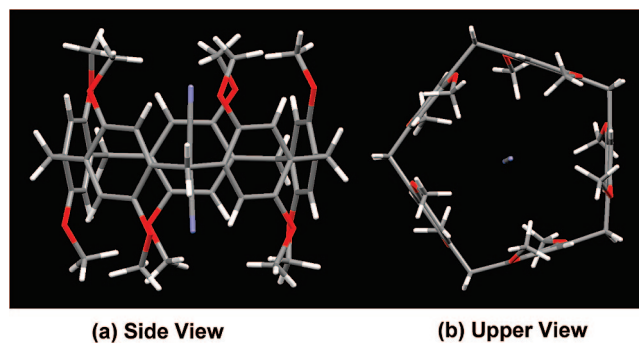
Calixarenes are *meta*-bridged phenolic macrocycles and form interesting vase-shape architecture.<sup>1</sup> Due to their characteristic structure, they have occupied well-established roles in supramolecular chemistry. Successful supramolecular platforms based on calixarenes for the synthesis of versatile and efficient receptors were reported by Ungaro, Reinhoudt, and co-workers.<sup>2</sup> However, because they form various structural isomers and vase-shape structure, calixarenes themselves are not enough to form stable inclusion complexes with guests compared with the other macrocycles, such as cyclodextrins<sup>3</sup> and cucurbiturils.<sup>4</sup> By introducing functional groups into upper and/or lower rim of calixarenes, functionalized calixarenes are able to stably include guests into their cavity.<sup>5</sup>

Herein, we report on *para*-bridged pillar-shaped novel hosts, “pillar[5]arenes”. By condensation of 1,4-dimethoxybenzene (DMB) with paraformaldehyde and an appropriate Lewis acid as a catalyst, the symmetrical host of 1,4-dimethoxypillar[5]arene (DMpillar[5]arene) was selectively obtained (Scheme 1). Composition of pillar[5]arenes is almost analogous to typical calixarenes. However, DMB units are connected by methylene bridges at the 2 and 5 positions. Therefore, structure of pillar[5]arene is a symmetrical pillar architecture, while typical calixarenes form a basket structure.

By using various Lewis acids, condensation of DMB with paraformaldehyde was examined (Scheme 1). Typical GPC traces after the condensation are shown in Figure 1. By using sulfuric acid, aluminum(III) chloride, iron(III) chloride (Figure 1a), titanium chloride, and tin(IV) chloride (Figure 1b) as catalyst, both a broad peak at an elution volume from 17 to 21 mL and a sharp peak at an elution volume of 22 mL were observed. The broad and sharp peaks resulted from polymer and a particular oligomer of DMB, respectively. On the other hand, using boron trifluoride diethyl etherate [BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>] (Figure 1c), the sharp peak at 22 mL was mainly seen. These observations indicate that the particular oligomer is selectively obtained by using BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (yield: 22.0%). The product by using BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> was successfully recrystallized with acetonitrile. From X-ray crystallography (Figure 2), it was confirmed that the crystalline structure was a cyclic pentamer of DMB (DMpillar[5]arene). DMB units in DMpillar[5]arene were connected by methylene bridges at the 2 and 5 positions. Structure of DMpillar[5]arene was an equilateral pentagon from the upper view and a symmetrical pillar structure from the side view. The linkage of the methylene bridge at the 2 and 5 positions of DMB in DMpillar[5]arene results in the interesting symmetrical structure. In contrast, typical calixarenes form vase-shaped architecture due to methylene bridges at their *meta*-position. Therefore, the structure of DMpillar[5]arene is different from that of typical calixarenes (detailed comparison of the structures between DMpillar[5]arene and *p*-*tert*-calix[6]arene is shown in Supporting

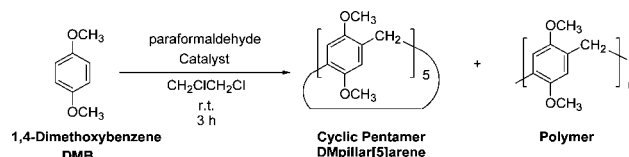


**Figure 1.** GPC traces of the obtained products using (a) FeCl<sub>3</sub>, (b) SnCl<sub>4</sub>, and (c) BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> as a Lewis acid.



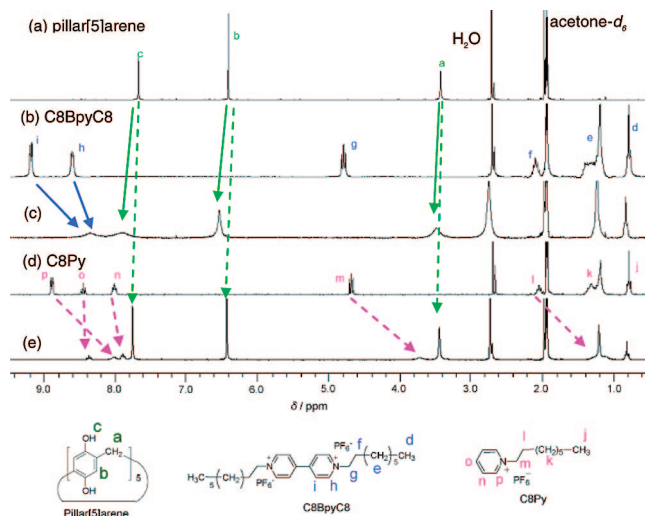
**Figure 2.** Crystal structure of DMpillar[5]arene from the side (a) and upper view (b).

**Scheme 1.** Condensation of 1,4-Dimethoxybenzene with Lewis Acids



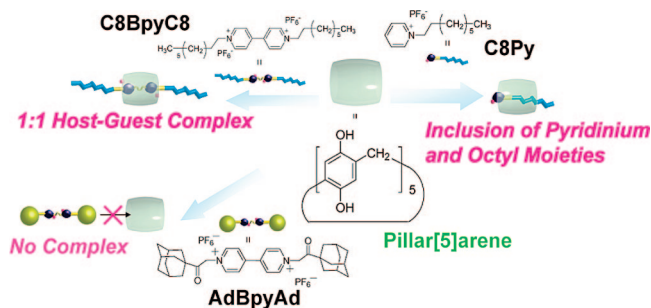
Information). Furthermore, in the X-ray crystal structure of DMpillar[5]arene, acetonitrile was included in the cavity of DMpillar[5]arene. The diameter of the cavity of DMpillar[5]arene was ca. 5 Å. Cavity size of DMpillar[5]arene is almost analogous to that of α-cyclodextrin.<sup>3</sup>

Although DMpillar[5]arene is soluble in organic solvents such as chloroform, acetone, acetonitrile, THF, DMF, and DMSO, solubility of DMpillar[5]arene in these solvents is not very high due to its high crystallinity. To improve its solubility and increase functionality, a cyclic pentamer of hydroquinone (pillar[5]arene, Scheme 2) was prepared from DMpillar[5]arene (yield: 30%). Compared with DMpillar[5]arene, pillar[5]arene showed excellent solubility in methanol, acetone, acetonitrile, DMF, and DMSO.



**Figure 3.**  $^1\text{H}$  NMR spectra of pillar[5]arene (a), C8BpyC8 (b), the mixture of pillar[5]arene and C8BpyC8 (c), C8Py (d), and the mixture of pillar[5]arene and C8Py (e) in 5 mM in acetone- $d_6$  at 25 °C.

**Scheme 2.** Host–Guest Complexes of Pillar[5]arene with C8BpyC8, C8Py, and AdBpyAd



To examine the conformation of pillar[5]arenes, variable-temperature  $^1\text{H}$  NMR measurements were carried out. In typical calixarenes, proton signals of the methylene bridge were split at low temperature because these methylene protons were distinguishable.<sup>1</sup> In contrast, in pillar[5]arenes, proton signals were not split even at  $-50$  °C (Supporting Information), indicating that proton signals of pillar[5]arenes were not distinguished due to their high symmetrical structures.

Since pillar[5]arene is symmetric by comparison with typical calixarenes, pillar[5]arene should capture guests into the cavity without modifications. Pillar[5]arene is composed of an electron donor of hydroquinone and has ionophore at both ends, thus the symmetric electron acceptor of dioctyl viologen salt (C8BpyC8) was employed as a guest molecule.  $^1\text{H}$  NMR spectrum of the mixture of pillar[5]arene and C8BpyC8 is shown in Figure 3c. The peaks of the viologen groups (peaks h and i) showed large upfield shifts, whereas the proton resonance band attributed to the methyl group (peak d) of C8BpyC8 exhibited no significant shifts. These observations indicate that the viologen group of C8BpyC8 was included into the cavity of pillar[5]arene.<sup>6</sup> In the case of a typical calixarene, formation of the host–guest complexes with C8BpyC8 was not observed (Supporting Information). When diadamantyl viologen salt (AdBpyAd) was used as a guest instead of C8BpyC8, these peak shifts and broadening were not observed (Supporting Information). Since the bulky adamantyl group of AdBpyAd was unable to thread the cavity of pillar[5]arene, the pillar[5]arene–AdBpyAd complex did not form. By mixing octyl pyridinium

salt (C8Py) with pillar[5]arene, proton signals derived from the 2 position of pyridinium (peak p) and methylene signals (peaks m and l) exhibited large upfield shifts compared with the other protons (Figure 3e), indicating that both the pyridinium cation and the methylene moieties of C8Py were included into the pillar[5]arene cavity.<sup>7</sup>

In conclusion, a new symmetrical host, pillar[5]arene, was obtained via a Lewis acid catalyzed procedure. Pillar[5]arene formed inclusion complexes with viologen and pyridinium derivatives due to its symmetrical structure. Host–guest property of pillar[5]arene is analogous to that of cucurbiturils.<sup>4</sup> Since pillar[5]arene has reactive hydroxyl groups at both ends, which is the same as cyclodextrins, pillar[5]arene should be easily functionalized. Therefore, we believe that pillar[5]arene will enlarge host–guest chemistry and should be used as new hosts. Future works will focus on host–guest chemistry of pillar[5]arene and use of pillar[5]arene as a wheel for construction of rotaxanes, catenanes, and supramolecular polymers with viologen derivatives because the adamantyl group acts as a bulky stopper of pillar[5]arene.

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**Supporting Information Available:** Experimental section,  $^1\text{H}$ ,  $^{13}\text{C}$ , and variable-temperature  $^1\text{H}$  NMR spectra of DMpillar[5]arene and pillar[5]arene, X-ray crystallographic data in CIF format, ORTEP drawing of DMpillar[5]arene, structures of DMpillar[5]arene and calix[6]arene, Job plots, MALDI-TOF mass spectrum of the host–guest complex of C8BpyC8 with pillar[5]arene, and  $^1\text{H}$  NMR spectra of C8BpyC8 with *p*-*tert*-butylcalix[6]arene and AdBpyAd with pillar[5]arene, determination of the association constants from fluorescence measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) The stoichiometry of the host–guest complex of C8BpyC8 with pillar[5]arene was determined by Job plots and MALDI-TOF mass measurement. Job plots and MALDI-TOF mass measurement confirmed the assumed 1:1 stoichiometry of the inclusion complex. Association constant of the pillar[5]arene–C8BpyC8 complex in methanol determined by fluorescence measurements was  $(1.2 \pm 0.2) \times 10^4 \text{ M}^{-1}$  (Supporting Information).
- (7) Formation of 1:1 host–guest complex of C8Py with pillar[5]arene was checked by Job plots. Association constant of the pillar[5]arene–C8Py complex in methanol determined by fluorescence measurements was  $(1.2 \pm 0.3) \times 10^3 \text{ M}^{-1}$  (Supporting Information).

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