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Conversion from Pillar[5]arene to Pillar[6–15]arenes by Ring Expansion and Encapsulation of C_{60} by Pillar[*n*]arenes with Nanosize Cavities

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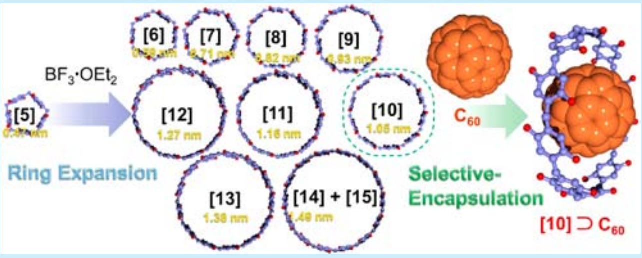
Supporting Information

ABSTRACT: Conversion of ring size from pillar[5]arene to pillar[6–15]arenes and isolation of pillar[*n*]arene homologues (*n* = 11–13) with known pillar[*n*]arene homologues (*n* = 6–10) are demonstrated. Pillar[10]arene formed the most stable host–guest complex with C_{60} among the pillar[5–14]arenes.



The host–guest chemistry between macrocyclic hosts and fullerenes[1−7] was first investigated using traditional hosts such as calix[*n*]arenes,[2] cucurbit[7]uril,[3] and cyclodextrins[4] and has been extensively studied using new macrocyclic molecules[5−7] including cycloparaphenylenes[5] and paraphenylene-acetylenes.[6] The van der Waals diameter of the smallest fullerene, buckminster fullerene (C_{60}), is 1.01 nm; therefore, a large cavity of over 1 nm in diameter is needed for macrocyclic hosts to encapsulate fullerenes.

Pillar[*n*]arenes,[8−12] first reported by our group in 2008,[8] are new macrocyclic hosts at the core of supramolecular chemistry. Pillar[5]arenes are cyclic pentamers that were first prepared by reacting 1,4-dialkoxybenzene with paraformaldehyde in the presence of $BF_3·OEt_2$ in 1,2-dichloroethane. Using 1,2-dichloroethane as a solvent, pillar[5]arenes were obtained selectively from other pillar[*n*]arene homologues (Figure 1a).[8,10] This is because 1,2-dichoroethane is included in the cavity of pillar[5]arenes and acts as template solvent to promote the formation of pillar[5]arenes,[11] indicating that the reaction proceeds under thermodynamic control. In contrast, larger pillar[*n*]arene homologues (*n* = 6–10) can be obtained using chloroform as a solvent. Hou et al. prepared pillar[*n*]arene homologues **C2[5–10]** in chloroform (Figure 1b).[12] Mixtures of **C2[5–10]** are obtained by controlling the reaction time; thus, the reaction is under kinetic control. Unlike in the case of 1,2-dichoroethane, chloroform does not act as a template.[11] In this study, we expanded the ring size of pillar[5]arene to pillar[*n*]arene homologues with larger cavities. Conversion of cyclic pentamer **C2[5]** enabled us to obtain a mixture of **C2[5–15]** and isolate new pillar[*n*]arene homologues **C2[11–13]** with nanosize cavities in addition to known pillar[*n*]arene homologues **C2[6–10]**. Encapsulation of C_{60} was investigated using pillar[*n*]arene homologues with various cavity sizes from 0.47 to 1.49 nm.[13]

C2[5] was used as a monomer for the syntheses of **C2[*n*]** homologues with larger cavities. **C2[5]** can be prepared in 1,2-dichoroethane by a one-step reaction under thermodynamic control (Figure 1a);[10b] therefore, it is a useful starting compound. First, **C2[5]** and $BF_3·OEt_2$ were dissolved in chloroform. The conversion of **C2[5]** to **C2[*n*]** did not proceed at 25 °C, but proceeded at 50 °C (Figure 1c). Heating is necessary for the ring-opening reaction to proceed. We monitored the conversion by ESIMS, ^{1}H NMR, and GPC measurements. The ESIMS spectrum (Figure 1d) shows that each signal appears at intervals of 178 amu (the constituent unit of pillar[*n*]arene) and that there are no other polymers and oligomers. From ^{1}H NMR and GPC measurements (Figure S5), the mixture of **C2[5–15]** was detected, but soluble byproducts such as linear polymers and oligomers were not. Thus, the conversion mainly afforded a mixture of pillar[*n*]-arene homologues. Chloroform cannot act as a template solvent for particular pillar[*n*]arenes; therefore, the reaction afforded the mixture of various pillar[*n*]arene homologues. After 1 h, an insoluble polymer formed in the mixture. This insoluble polymer should be formed by cross-linking between pillar[*n*]arenes. The amount of insoluble polymer increased with the reaction time. The reaction time was therefore one of

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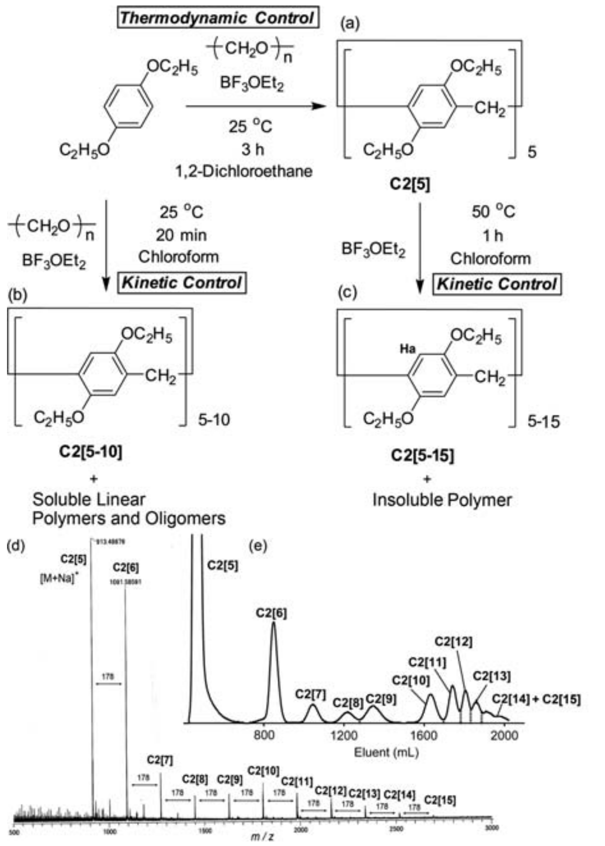

Figure 1. Synthesis of (a) pillar[5]arene **C2[5]** and (b) pillar[5–10]arenes **C2[5–10]** from 1,4-diethoxybenzene and (c) pillar[5–15]arenes **C2[5–15]** from **C2[5]**. (d) ESIMS spectrum of the mixture after the conversion reaction for 5 min. (e) Chromatogram of the mixture after the conversion reaction for 1 h.

the most important factors for the formation of **C2[5–15]**, which indicates the conversion reaction proceeded under kinetic control.[11] The reaction temperature is also an important factor for the ring-expansion reaction. The ring-expansion reaction at 80 °C led to an increased amount of insoluble polymer than that at 50 °C. The formation of the insoluble polymer led to a low yield of the mixtures of **C2[5–15]**; therefore, 1 h and 50 °C were optimal as the reaction time and temperature for the synthesis of larger pillar[*n*]arene homologues **C2[11–15]**. The products after the reaction were only a mixture of **C2[5–15]** and the insoluble polymer and did not contain soluble linear polymers or oligomers. As a result, we could obtain a mixture of **C2[11–15]** and then isolate each pillar[*n*]arene homologues by column chromatography with silica gel (Figure 1e), which gave unreacted starting compound **C2[5]** (yield: 26%, which can be used for the conversion again), **C2[6]** (yield: 3%), **C2[7]** (yield: 0.6%), **C2[8]** (yield: 0.5%), **C2[9]** (yield: 0.7%), **C2[10]** (yield: 1%), **C2[11]** (yield: 0.9%), **C2[12]** (yield: 0.3%), **C2[13]** (yield: 0.7%), and the tenth fraction containing **C2[14]** as a major and **C2[15]** as a minor product.[14] The yields of **C2[5–13]** are poor, but the formation of soluble byproducts such as linear polymers and oligomers is avoided. The lack of soluble byproducts enabled us to separate **C2[5–13]**. In contrast, the reaction using 1,4-diethoxybenzene and paraformaldehyde under the same reaction conditions afforded only soluble linear polymers (Figure S6). Even under the optimized conditions reported by Hou and co-workers,[12] the mixture contained both **C2[5–15]** and soluble linear polymers and oligomers (Figure S7), as they reported. Formation of soluble linear polymers and oligomers makes it difficult to isolate pillar[*n*]arene homologues because the solubility, polarity, and molecular weight of the linear polymers and oligomers are very similar to those of large pillar[*n*]arene homologues.

The series **C2[5–14]** possess different cavity sizes in the range from 0.47 to 1.49 nm; therefore host–guest complexation with C_{60} (van der Waals diameter of 1.01 nm) was investigated. The interaction between each pillar[*n*]arene and C_{60} was first investigated by ^{1}H NMR spectroscopy (Figure 2).

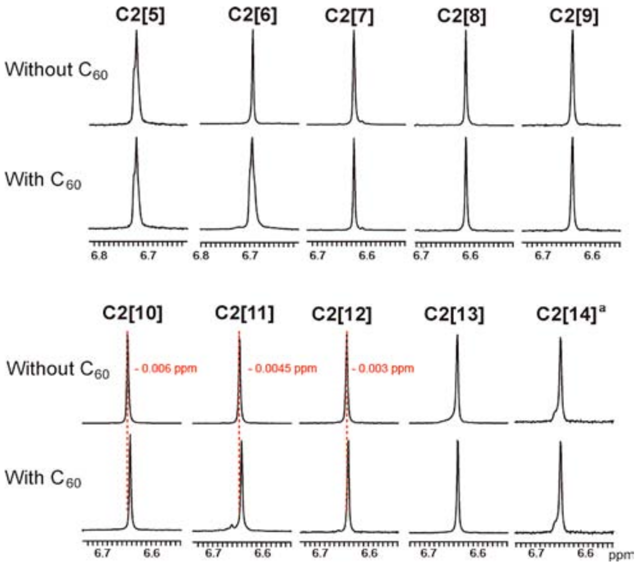

Figure 2. Partial ^{1}H NMR spectra of the signal from phenyl proton (Figure 1c, H_a) of **C2[5–14]** with and without C_{60}, $[C_{60}]$ = 0.022 mM, [**C2[5–14]**] = 0.45 mM in $CDCl_3$ at 25 °C. [a] **C2[14]** containing small amount of **C2[15]** was used.

When C_{60} was mixed with **C2[10]**, the proton signal for the benzene moiety of **C2[10]** (Figure 1c, H_a) showed the change in chemical shift (−0.0060 ppm). Similar chemical shift changes were observed in the cases of **C2[11]** and **C2[12]**, but the magnitudes of the shifts were relatively small (−0.0045 ppm for **C2[11]** and −0.0030 ppm for **C2[12]**). The same chemical shift changes for the proton peaks were observed in the cases of cycloparaphenylenes[5a] and paraphenylacetylene[6a] upon encapsulation of C_{60}. These results indicate encapsulation of C_{60} in the cavities of **C2[10–12]**. In contrast, when excess C_{60} was mixed with **C2[5–9]**, **C2[13]**, and **C2[14]** containing a small amount of **C2[15]**, no peak shifts were observed, indicating no encapsulation of C_{60} by **C2[5–9]** and **C2[13,14]**. The cavity sizes of **C2[10–12]** are similar to the van der Waals diameter of C_{60}; thus, C_{60} selectively forms host–guest complexes with **C2[10–12]** but not with **C2[5–9]** and **C2[13,14]**.

Formation of host–guest complexes of C_{60} with **C2[10–12]** was also studied by UV titration (Figure 3a). 1,1,2,2-Tetrachloroethane was used as a solvent because it is a better solvent for C_{60} than chloroform.[15] Upon addition of **C2[10]** to C_{60}, the absorption spectra of C_{60} changed. Clear isosbestic points were found at 406 and 476 nm, indicating 1:1 host–guest stoichiometry for **C2[10]** and C_{60}. The association constant between **C2[10]** and C_{60} in 1,1,2,2-tetrachloroethane determined by UV titration was (4.3 ± 0.3) × 10^2 M^{-1} (Figure S8). We also examined host–guest complexation by **C2[11]**

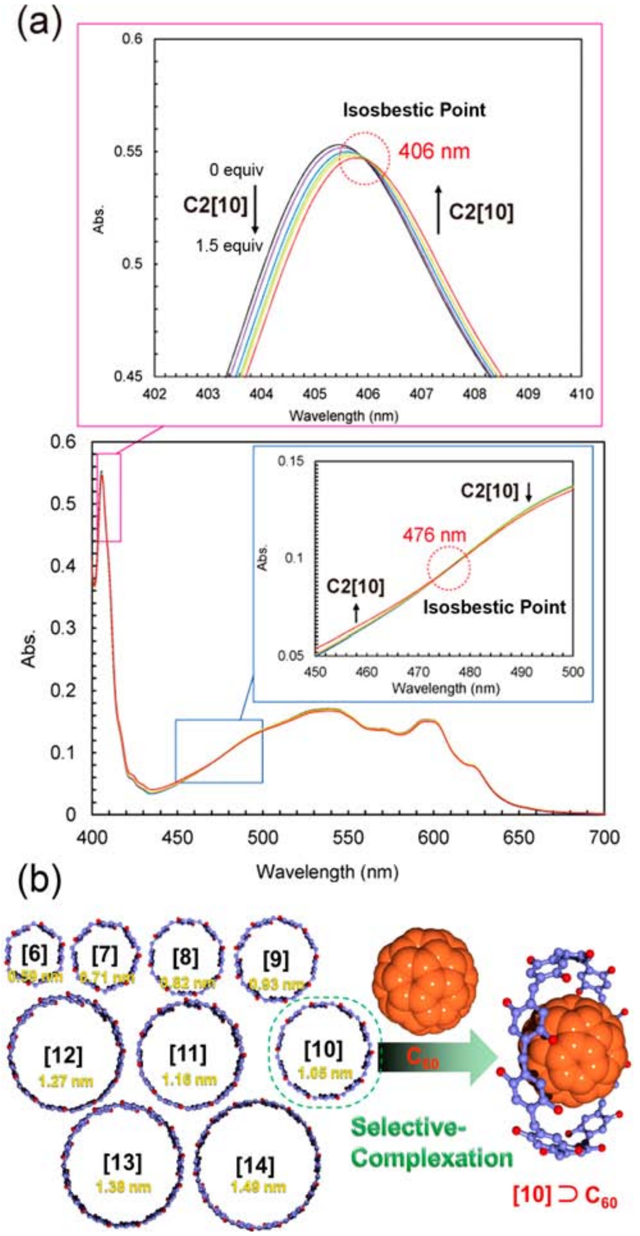

Figure 3. (a) UV−vis absorption spectra of C_{60} (38.5 μM) with various amounts of **C2**[**10**] ([**C2**[**10**]] = 0−100 μM) in 1,1,2,2-tetrachloroethane and the expanded spectra in the regions from 402 to 410 nm and from 450 to 500 nm. Arrows indicate the changes in absorption upon addition of **C2**[**10**]. (b) Size-selective encapsulation of C_{60} by **C2**[**10**].

and **C2**[**12**] using the same UV titration method. However, the binding with C_{60} was too weak to determine accurate association constants and isosbestic points (Figure S9). **C2**[**10**] therefore forms the most stable complex with C_{60} among **C2**[**5−14**]. The cavity size of **C2**[**10**] is 1.05 nm (in van der Waals diameter), which is sufficient for including C_{60} with a van der Waals diameter of 1.01 nm (Figure 3b). Cyclic compounds containing nanoscale oxaarenecyclynes (1.1−1.3 nm in diameter),[7] [10]cycloparaphenylene (1.38 nm in diameter),[5a] and [6]paraphenyleneacetylene (1.32 nm in diameter)[6a] form 1:1 host−guest complexes with C_{60}; thus encapsulation of C_{60} by **C2**[**10**] seems reasonable. The association constant between **C2**[**10**] and C_{60} in toluene was also determined by UV titration (Figure S10). The association constant was $(2.1 \pm 0.2) \times 10^3$ M^{-1}, which is about five times larger than that in 1,1,2,2-tetrachloroethane. The solubility of C_{60} in toluene is lower than that in 1,1,2,2-tetrachloroethane; thus, the lyophobic effect enhanced the stability of the host−guest complex in toluene. The association ability of **C2**[**10**] is in the same range or higher than those of previous macrocyclic hosts.[1−4,7]

In conclusion, we expanded the ring size of pillar[5]arene to produce pillar[6−15]arenes under kinetic control. The developed method enabled us to isolate pillar[*n*]arene homologues **C2**[**11−13**] with nanosize cavities. The merit of this method is the easy isolation of pillar[*n*]arene homologues because no soluble byproducts are formed. The mechanism of the conversion reaction is now under consideration. We investigated the ability of the series of pillar[*n*]arene homologues to selectively encapsulate C_{60} and found that **C2**[**10**] had the highest affinity for C_{60} among them. Therefore, pillar[*n*]arenes join the group of macrocyclic hosts that can encapsulate C_{60}. This study is a starting point for encapsulation of nanomaterials such as nanocarbons and nanoparticles and the construction of fullerene-based supramolecular assemblies using pillar[*n*]arenes with nanosize cavities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section; characterization data; ^{1}H NMR, ESIMS spectra; and GPC traces of the reaction mixtures using **C2**[**5**] and 1,4-diethoxybenzene as a starting compound and UV titrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) In crystalline states, pillar[8−10]arenes has two cavities (ref 12) because the cyclic pentagonal structure is geometrically stable. However, in solution states, they can form various conformations because flipping of the units takes places and the C−CH_2−C angle at the methylene linkers becomes wider and wider. Thus, we roughly calculated their diameters based on the diameter of the inscribed circle of the polygon.

(14) We carefully collected the tenth fraction, but the ESIMS spectrum showed a major peak from **C2**[**14**] and a minor peak from **C2**[**15**]. Thus, the fraction was a mixture of **C2**[**14**] containing a small amount of **C2**[**15**].

(15) Due to the low solubility of C_{60} for chloroform, we could not measure the UV changes of C_{60} upon addition of **C2**[**10**].