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# A New Calix[5]arene-Based Container: Selective Extraction of Higher Fullerenes

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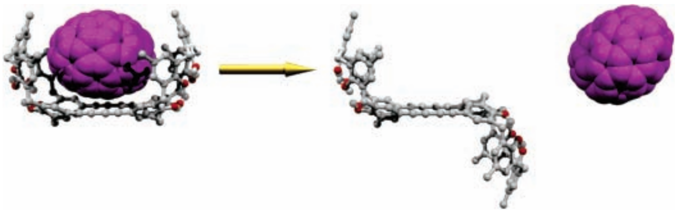
## ABSTRACT



**A new double calix[5]arene successfully extracts higher fullerenes from fullerene mixtures. The syn isomer of the double calix[5]arene selectively captures higher fullerenes from fullerene mixtures. The elevation of the temperature more than 100 °C stimulates its conformational change to the anti isomer, bringing liberation of the captured higher fullerenes.**

The fullerene family is one of the most intriguing classes of molecules and has received great attention due to potential applications in the fields of electrochemistry and material science.[1] Recent progress in the area of fullerene synthesis has provided an ample supply of $C_{60}$ for making extensive investigations into its physical, chemical, and biological properties.[2]

In contrast, these properties for higher fullerenes ($\geq C_{76}$) are not fully understood yet because of the difficulty of purification on a practical scale. Iterative chromatographic separation of higher fullerenes provides only a tiny amount of higher fullerenes.[3]

Recently, a useful method of purifying higher fullerenes using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) on a practical scale has been reported,[4] but the complexes formed with DBU are air-sensitive and need to be handled under an inert atmosphere.[4]

One method of purifying higher fullerenes is to utilize host−guest chemistry; however, there are limited examples of the encapsulation of higher fullerenes by artificial host molecules.[5] The selective formation of host−guest complexes between higher fullerenes and porphyrin dimers is one of the most successful examples.[6] Previously, we have reported that calix[5]arenes and their derivatives show high binding abilities for $C_{60}$ and/or $C_{70}$.[7] On the basis of these findings, fullerene container $\mathbf{1_s}$ was newly designed for higher fullerenes. In this paper we describe the synthesis of new

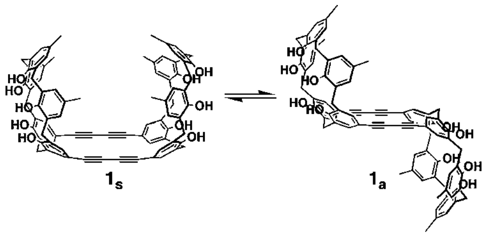


**Figure 1.** Two possible conformational isomers, $\mathbf{1_s}$ and $\mathbf{1_a}$.

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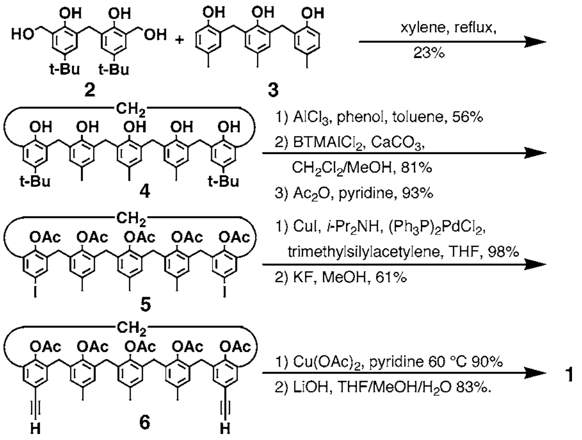
fullerene container **1**, its unique conformational behavior, and its selective extraction of higher fullerenes. The connection of the two calix[5]arene moieties with the two 1,3-butadiyne bridges makes the two conformational options $\mathbf{1_s}$ and $\mathbf{1_a}$. The concave cavity of $\mathbf{1_s}$ should be complementary to fullerenes larger than $C_{60}$ and $C_{70}$. Compared to $\mathbf{1_s}$, the other isomer $\mathbf{1_a}$ provides smaller binding abilities for the higher fullerenes because of the anti conformation. If the syn-anti conformational interconversion can be controlled by external stimuli, the binding ability of **1** toward higher fullerenes can be regulated through the uptake and release of higher fullerenes.

The synthesis of the container is outlined in Scheme 1.

**Scheme 1.** Synthesis of Double Calix[5]arene **1**



Cyclization of **2**[8] and **3**[9] under reflux afforded calix[5]arene **4** in 23% yield. Removal of *tert*-butyl groups with aluminum chloride and phenol, followed by iodination with benzyltrimethylammonium iododichloride, and protection of five phenolic hydroxyl groups with acetic anhydride furnished diiodocalix[5]arene **5**. Following Sonogashira coupling of **5** with trimethylsilylacetylene under palladium catalysis, deprotection of the trimethylsilyl group produced diethynyl calix[5]arene **6** in good yield. Eglinton coupling of **6** in the presence of copper acetate at 60 °C worked nicely, and the following deprotection of the five acetyl groups furnished the desired double calix[5]arene **1** in excellent yield.

Two sets of aromatic signals assigned to protons $H_a$ and $H_b$ appeared with unequal intensities, suggesting that two conformational isomers exist in a ratio of 7:3 (Figure 2a). The minor signals of $H_a$ and $H_b$ increased along with an increase in the temperature (Figure 2b,c). At 130 °C, the relative population of the two isomers was almost equal. The signal intensities of the two isomers did not change when the solution was cooled to 25 °C: the population of the two isomers was still almost equal at 25 °C (Figure 2d). These results indicate that a sizable energetic barrier between the isomers exists and they are atropisomers.

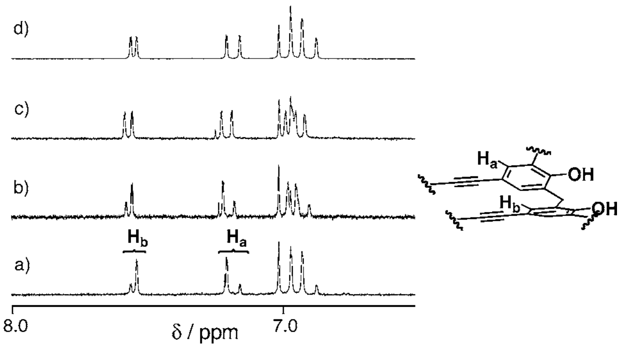


**Figure 2.** $^1$H NMR spectra of **1** at (a) 298 K, (b) 363 K, (c) 403 K, and (d) cooling to 298 K in tetrachloroethane-$d_2$.

Luckily, the solubility of the two isomers are very different from each other in toluene. A simple washing of a 1:1 mixture of the two isomers with toluene gave compound $\mathbf{1_a}$ from the filtrate. The other isomer $\mathbf{1_s}$ was obtained from the residual solid. Even such a simple procedure gave satisfactory separation of the two isomers (Figure 3).

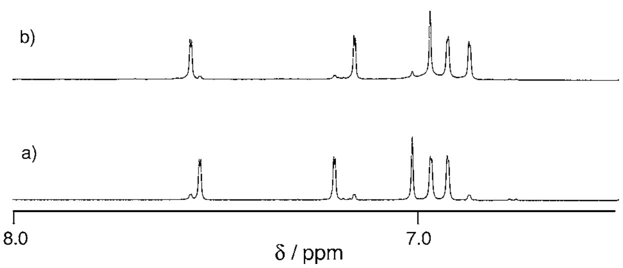


**Figure 3.** $^1$H NMR spectra of (a) $\mathbf{1_s}$ and (b) $\mathbf{1_a}$ at 298 K in tetrachloroethane-$d_2$.

The reversible first-order rate constants of the isomerization reaction between $\mathbf{1_s}$ and $\mathbf{1_a}$ (Figure 4) were determined in a range of 60−90 °C, and an Eyring plot resulted in the activation parameters ($\Delta H^{\ddagger}$, 112 ± 2 kJ·mol$^{-1}$; $\Delta S^{\ddagger}$, −4 ±

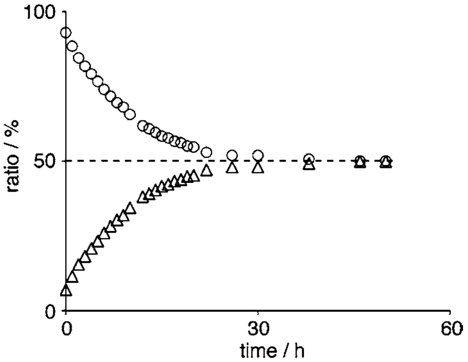


**Figure 4.** Time course of a relative ratio of $\mathbf{1_s}$ (○) and $\mathbf{1_a}$ (△) at 333 K in tetrachloroethane-$d_2$.

**Table 1.** Binding Constants ($K_a$) of $\mathbf{1_s}$ and **9** for Fullerenes at 298 K in 1,1,2,2-Tetrachloroethane

| host | $K_a$ ($M^{-1}$) | | | | |
|---|---|---|---|---|---|
| | $C_{60}$ | $C_{70}$ | $C_{76}$ | $C_{78}$ | $C_{84}$ |
| $\mathbf{1_s}$ | 9700 ± 100 | 29000 ± 2000 | 90000 ± 10000 | 110000 ± 20000 | 20000 ± 2000 |
| **9** | 1550 ± 40 | 2800 ± 100 | 1850 ± 70 | 2500 ± 200 | 110 ± 10 |

6 J·mol$^{-1}$·K$^{-1}$). On the basis of the activation parameters, the half-life of the isomers is about 32 days at 25 °C whereas it is about 26 s at 130 °C.

The determination of the structures of the isomers $\mathbf{1_s}$ and $\mathbf{1_a}$ was carried out by Job's plots. The Job's plot of isomer $\mathbf{1_s}$ with $C_{60}$ gave a maximum at a 1:1 molar ratio, indicating that $\mathbf{1_s}$ adopts the syn conformation. In contrast, a peak of the plot for $\mathbf{1_a}$ appeared at a molar fraction of 0.6, which indicated the formation of 2:1 host−guest complex $\mathbf{1_a}\cdot\mathbf{1_a}\supset C_{60}$ (Figure 5a).

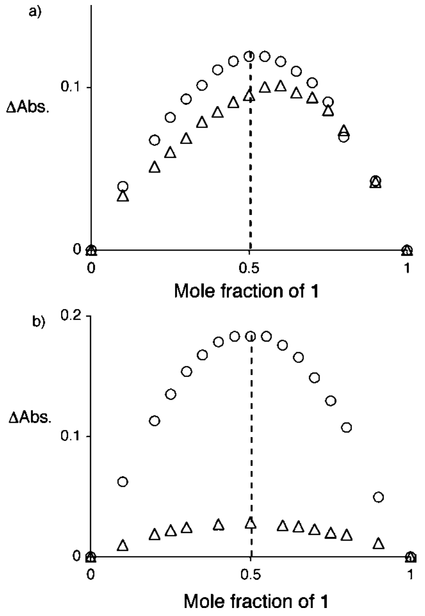
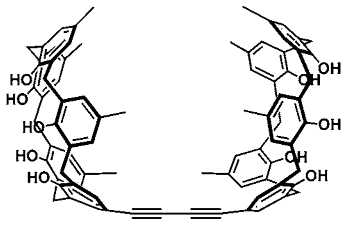


**Figure 5.** Job's plots of (a) $C_{60}$ with $\mathbf{1_s}$ (○) or $\mathbf{1_a}$ (△) and (b) **7** with $\mathbf{1_s}$ (○) or $\mathbf{1_a}$ (△) in tetrachloroethane-$d_2$.

This interesting observation suggested that two $\mathbf{1_a}$ molecules come together to cover up a $C_{60}$ molecule using one of the two calix[5]arene units of $\mathbf{1_a}$, meaning that the complexation of a $C_{60}$ molecule to one of the two calix[5]arenes reduces the binding ability of the other. Job's plots for $\mathbf{1_s}$ and $\mathbf{1_a}$ with diethyl-1,2-methano[60]fullerene-61,61-dicarboxylate **7**[10] were carried out again. The bis(diethoxylcarbonyl)methylene group of **7** should be able to interfere with the formation of the 2:1 host−guest complex with $\mathbf{1_a}$ as a result of the steric hindrance of the substituent. As expected, both $\mathbf{1_s}$ and $\mathbf{1_a}$ showed 1:1 host−guest complexes with **7** (Figure 5b). The binding constants of **1** toward **7** were compared to that of 5,11,17,23,29-pentamethylcalix[5]arene **8**[11] ($K_a$ 2670 ± 40 $M^{-1}$ for $\mathbf{1_s}$; 433 ± 9 $M^{-1}$ for $\mathbf{1_a}$; 251 ± 4 $M^{-1}$ for **8**). The binding constant of $\mathbf{1_a}$ to **7** is close to that of **8**. In contrast, the binding constant of $\mathbf{1_s}$ is six times as large as that of $\mathbf{1_a}$. The binding constants clearly indicate that $\mathbf{1_s}$ has syn conformation whereas $\mathbf{1_a}$ does not.

The binding constants to higher fullerenes of $\mathbf{1_s}$ and **9**[7g] were determined in 1,1,2,2-tetrachloroethane (Figure 6, Table 1). The binding constants of $\mathbf{1_s}$ to the fullerene molecules are higher compared with those of **9**, and the selectivity of $\mathbf{1_s}$ for the higher fullerene molecules relative to $C_{60}$ and $C_{70}$ dramatically increased. It is obvious that the well-preorganized cavity composed of the two calix[5]arenes of $\mathbf{1_s}$ provides the binding environment complementary to the exterior of the higher fullerenes.



**9**

**Figure 6.** Reference host **9**.

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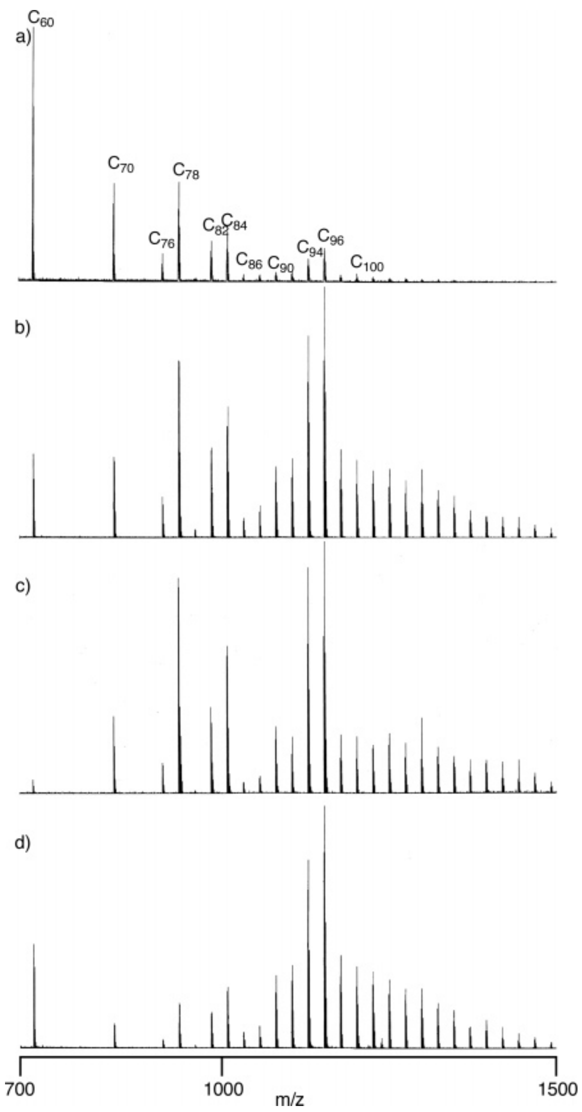

**Figure 7.** MALDI-TOF mass spectra of (a) fullerene mixture, (b) first extracts, (c) second extracts, (d) the residue of the second extraction.

Practical extraction of the higher fullerene was carried out using a fullerene mixture, containing $C_{60}$ (67%), $C_{70}$ (23%), and higher fullerenes (10%) (Figure 7a). A toluene solution of the fullerene mixture (300 mg) and $\mathbf{1_s}$ (40 mg) was stirred for 1 h, and the precipitates of the host−guest complex of $\mathbf{1_s}$ with fullerenes formed. The precipitates were heated at 100 °C in 1,1,2,2-tetrachloroethane for a while. Heating at 100 °C accelerated the isomerization of $\mathbf{1_s}$ to anti conformer $\mathbf{1_a}$, quickly releasing the captured fullerenes, and then a hot solution of them was quickly passed through alumina column to give a first extract, containing a higher fullerene enriched mixture (8.3 mg) (Figure 7b).

Repeating this procedure for the first extracts with $\mathbf{1_s}$ (4 mg) furnished a higher fullerene mixture (4.85 mg) and successfully excluded $C_{60}$ (Figure 7c). The residual solution gave a higher fullerene mixture (3.0 mg) that mainly includes fullerene molecules larger than $C_{90}$.

In summary, we demonstrated the synthesis of a new upper-rim bridged double-calix[5]arene, which gave rise to syn and anti conformations. The energetic barrier of the interconversion between them is quite high, and they are atropisomeric at room temperature. The elevation of the temperature higher than 60 °C accelerates the rate of the interconversion. Syn conformer $\mathbf{1_s}$ shows extremely high binding abilities for higher fullerenes and precipitates with higher fullerenes as host−guest complexes. The captured fullerenes are released by heating to afford an enriched higher fullerene mixture on a practical scale.

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**Supporting Information Available:** Experimental procedures, spectral data for all new compounds, time course of $^1$H NMR spectrum changes for the syn-anti somerization at 333 K, Eyring plot, and HPLC data of the extracts. This material is available free of charge via the Internet at http://pubs.acs.org.

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