

Self-inclusion properties of C₆₀-linked calix[5]arene

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Abstract—C₆₀-linked calix[5]arenes were synthesized and their intramolecular binding properties were investigated. The self-inclusion ratio of the C₆₀ moiety was determined by using UV–vis spectroscopy, and the ratio depends on chain length, temperature, and solvent. Influence of temperature and solvent was explained by the thermodynamic data of the intramolecular complex formation process.

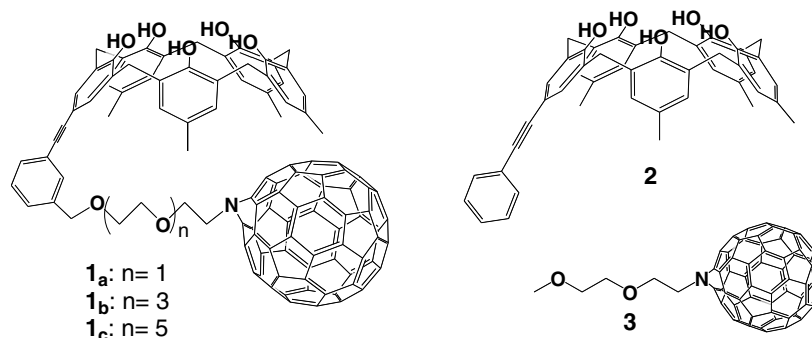
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Fullerene and its derivatives represent an intriguing class of molecules due to their unique physical and chemical properties.¹ Their applications have been intensively studied in many research areas such as chemistry, material science, biology, etc.² Developing specific receptors for fullerenes is of great interest in constructing fullerene-based functional materials. Recently, a lot of studies that focus on the inclusion of fullerenes in solution and solid state have been reported.³ In our previous paper, we have reported that calix[5]arenes and their derivatives can strongly bind C₆₀ in organic solvents, and in solid state.⁴ In order to gain the high ratio of the host–guest complex in solution, the concentration of the calix[5]arene hosts and C₆₀ must be increased; however, it sometimes cannot be attained due to the poor solubility of C₆₀. In general, molecular association of

two or more precursors should pay high entropic cost due to the restriction of their freedom of movement, causing the negative entropy change in the association process. However, intramolecular complex formation is advantageous to achieve rather high complexation ratio because of the reduction of the unfavorable entropic cost.

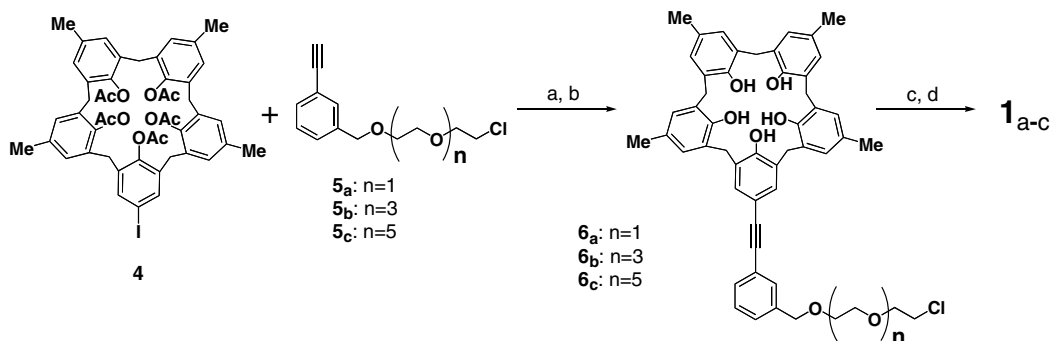
In order to gain high complexation ratio in solution, we tied C₆₀ to a receptor. This type of molecule was already prepared by Shinkai's group.⁵ We report here the synthesis and self-inclusion behaviors of C₆₀-linked calix[5]arene **1_{a-c}**.

Synthesis of C₆₀-linked calix[5]arene **1_{a-c}** is shown in Scheme 1. Sonogashira's coupling of **4** and **5_{a-c}**,



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Scheme 1. (a) CuI, *n*-butylamine, Pd(PPh₃)₄, THF; (b) K₂CO₃, MeOH/THF two steps 50–60%; (c) NaN₃, Me₂SO; (d) C₆₀, PhCl, two steps 20–40%.

followed by a removal of the acetyl groups gave calixarene derivatives **6**_{a–c} in good yield. Treatment of **6**_{a–c} by NaN₃ in DMSO afforded azide compounds. Reflux of the mixture of C₆₀ and the azides in chlorobenzene furnished target compounds **1**_{a–c} in 20–40% yield.⁶

The ¹H NMR spectra of **1**_{a–c} showed a broad AB-quartet like signal in 3.8–4.2 ppm assignable to the bridging methylene of the calix[5]arene at a millimolar concentration, indicating the slow inversion of a cone conformation to its mirror image at room temperature. Similar NMR signals were observed in an intermolecular inclusion complex of C₆₀ and a calix[5]arene host. In the free calix[5]arene host, the ring flipping process occurs rapidly at room temperature to give a broad singlet of the methylene signal. The AB-quartet like signal indicates that the energetic barrier to the ring flipping is increased by the complexation with the C₆₀ guest. The presence of the broad AB-quartet of **1** even in a diluted solution suggested that a high ratio of the complexed form in this intramolecular host–guest system. The ¹³C signals of the C₆₀ moiety of **1**_a shifted up-field from those of **3** in CDCl₃ at 298 K.⁷ The up-field shift values are about 0.8–1.3 ppm, which is consistent with those found in the 1:1 complex of C₆₀ and the calix[5]arenes.^{4a}

Absorption spectra of **1**_a, **3**, and a mixture of **2** and **3** in CHCl₃ are shown in Figure 1. In **1**_a, the intensity of the shoulder at 430–450 nm region increased, whereas 500–

650 nm region decreased when compared to those of **3**. Similar spectral changes were observed in the titration experiments with **2** and **3**, and the spectra have an isosbestic point at 495 nm. The spectrum of **1**_a also passes through this isosbestic point. The fact suggests that the binding manner of the intramolecular complex formation is quite similar to that of the intermolecular association between **2** and **3**. Thus, the ratio of the intramolecular complex formation can be estimated from the intensity of the absorbance at 432 nm of **1**_{a–c} by comparison with the calibration plots (Figs. 2 and 3), obtained by the titration experiment spectra of the intermolecular complex formation at 432 nm between **2** and **3**.

The ratios of the intramolecular complex formation are shown in Table 1. The complexation ratio is larger in all compounds than that of the intermolecular complex of **2** and **3** at the same concentration. The ratio is dependent on the chain length and the temperature. The remarkable solvent effect was observed between the CHCl₃ and toluene. In CHCl₃, the complexation ratios increased with decrease of the temperature. On the other hands, in toluene, the completely reverse binding behavior was observed; the ratio increased with the increase of the temperature. The inclusion ratio is found to be independent on the concentration of **1** at micro- to millimolar concentrations. This rules out the formation of the intermolecular dimer.

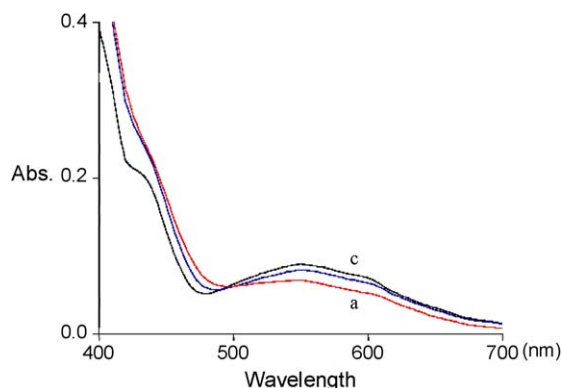


Figure 1. Absorption spectra of (a) **1**_a (6.20×10^{-2} mmol/L); (b) **2** (2.17 mmol/L); and (c) **3** (6.20×10^{-2} mmol/L) in CHCl₃ at 298 K.

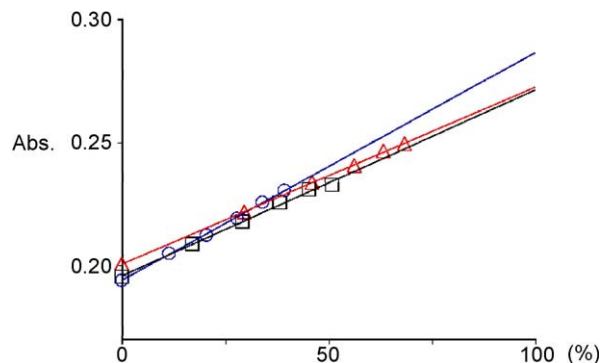


Figure 2. Plots of the intermolecular complexation ratio of **2** and **3** versus observed absorbance in CHCl₃ at 282 K (Δ), 303 K (□), and 320 K (○). The concentrations are [3] = 6.20×10^{-2} mmol/L and [2] = from left to right: 0.0, 4.40, 8.80, 13.2, 17.6, 22.0 × 10⁻¹ mmol/L.

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