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Tetrahedron Letters 46 (2005) 1411–1414

Tetrahedron Letters

Self-inclusion properties of C_{60}-linked calix[5]arene

Takeharu Haino,* Manabu Yanase and Yoshimasa Fukazawa*

Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8526, Japan

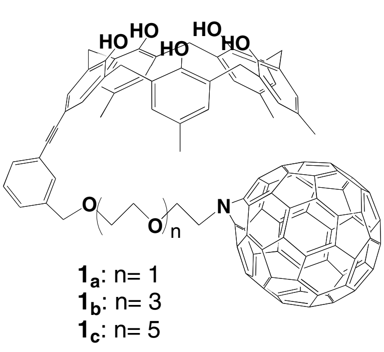
Received 15 December 2004; revised 6 January 2005; accepted 11 January 2005
Available online 25 January 2005

Abstract—C_{60}-linked calix[5]arenes were synthesized and their intramolecular binding properties were investigated. The self-inclusion ratio of the C_{60} 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.

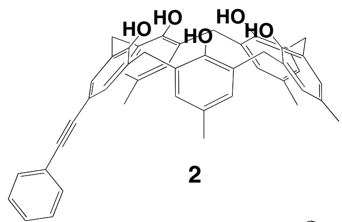
Fullerene and its derivatives represent an intriguing class of molecules due to their unique physical and chemical properties.[1] Their applications have been intensively studied in many research areas such as chemistry, material science, biology, etc.[2] Developing specific receptors for fullerenes 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 C_{60} 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 C_{60} must be increased; however, it sometimes cannot be attained due to the poor solubility of C_{60}. 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 C_{60} 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 C_{60}-linked calix[5]arene $\mathbf{1_{a-c}}$.

Synthesis of C_{60}-linked calix[5]arene $\mathbf{1_{a-c}}$ is shown in Scheme 1. Sonogashira's coupling of **4** and $\mathbf{5_{a-c}}$,



$\mathbf{1_a}$: n= 1
$\mathbf{1_b}$: n= 3
$\mathbf{1_c}$: n= 5



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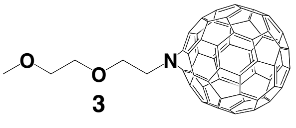

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Keywords: Fullerene; Calix[5]arene; Self-inclusion; Solvent effect; Thermodynamic study.

* Corresponding authors. Tel.: +81 82 424 7403; fax: +81 82 424 0724 (T.H.); e-mail addresses: haino@sci.hiroshima-u.ac.jp; fukazawa@sci.hiroshima-u.ac.jp

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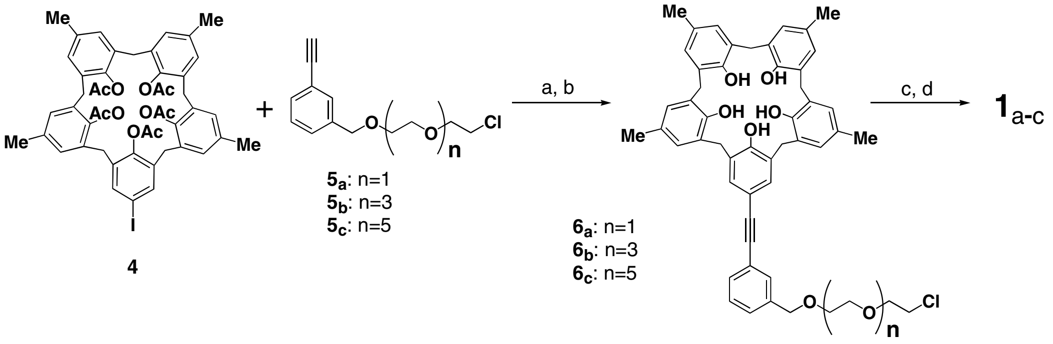
doi:10.1016/j.tetlet.2005.01.035



Scheme 1. (a) CuI, *n*-butylamine, Pd(PPh_3)$_4$, THF; (b) K_2CO_3, MeOH/THF two steps 50–60%; (c) NaN_3, Me_2SO; (d) C_{60}, PhCl, two steps 20–40%.

followed by a removal of the acetyl groups gave calixarene derivatives **6**$_{\mathbf{a-c}}$ in good yield. Treatment of **6**$_{\mathbf{a-c}}$ by NaN_3 in DMSO afforded azide compounds. Reflux of the mixture of C_{60} and the azides in chlorobenzene furnished target compounds **1**$_{\mathbf{a-c}}$ in 20–40% yield.[6]

The ^1H NMR spectra of **1**$_{\mathbf{a-c}}$ 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 C_{60} 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 C_{60} 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 ^{13}C signals of the C_{60} moiety of **1**$_{\mathbf{a}}$ shifted up-field from those of **3** in $CDCl_3$ 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 C_{60} and the calix[5]arenes.[4a]

Absorption spectra of **1**$_{\mathbf{a}}$, **3**, and a mixture of **2** and **3** in $CHCl_3$ are shown in Figure 1. In **1a**, 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**$_{\mathbf{a}}$ 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**$_{\mathbf{a-c}}$ 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 $CHCl_3$ and toluene. In $CHCl_3$, 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.

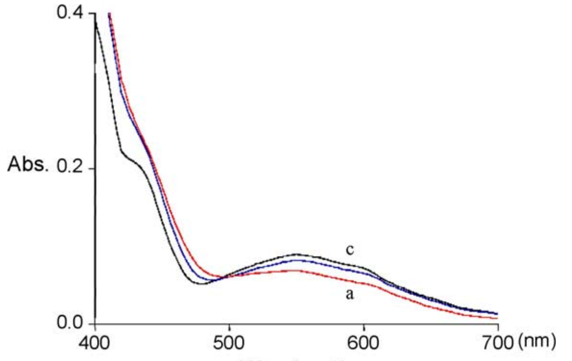


Figure 1. Absorption spectra of (a) **1a** (6.20×10^{-2} mmol/L); (b) **2** (2.17 mmol/L); and **3** (6.20×10^{-2} mmol/L); (c) **3** (6.20×10^{-2} mmol/L) in $CHCl_3$ at 298 K.

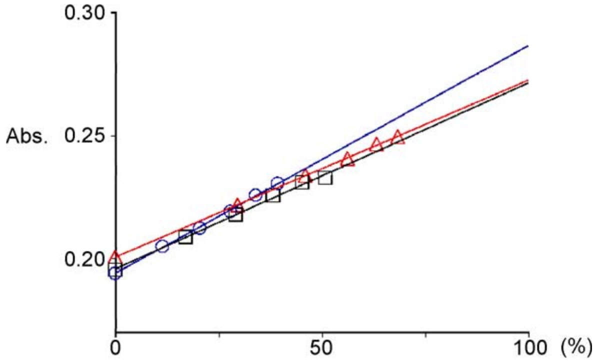


Figure 2. Plots of the intermolecular complexation ratio of **2** and **3** versus observed absorbance in $CHCl_3$ at 282 K (△), 303 K (□), and 320 K (○). The concentrations are [**3**] = 6.20×10^{-2} mmol/L and [**2**] = from left to right: 0.0, 4.40, 8.80, 13.2, 17.6, 22.0×10^{-1} mmol/L.

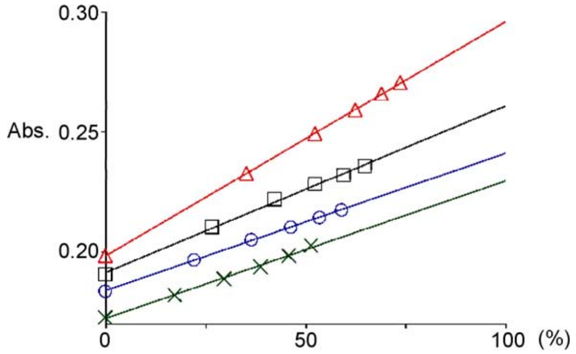


Figure 3. Plots of the intermolecular complexation ratio of **2** and **3** versus observed absorbance in toluene at 282 K (△), 303 K (□), 320 K (○), and 345 K (×). The concentrations are [**3**] = 5.72 × 10^{-2} mmol/L and [**2**] = from left to right: 0.0, 4.40, 8.80, 13.2, 17.6, 22.0 × 10^{-1} mmol/L.

Table 1. Inclusion ratio (%) of **1**–**3**

Temp (K)	CHCl$_3$				Toluene			
	1a	**1b**	**1c**	**2** and **3**[a]	**1a**	**1b**	**1c**	**2** and **3**[a]
345					84	71	48	2.6
320	62	43	26	2.1	78	63	40	3.6
303	80	58	35	3.0	66	53	35	4.4
282	90	68	44	5.9	50	41	23	6.4

[a] The complexation ratios of **2** and **3** at same concentration as **1a**–**c** were determined by UV–vis spectra at the concentrations (6.20 × 10^{-5} mol/L in CHCl$_3$, 5.63 × 10^{-5} mol/L in toluene).

Table 2. Thermodynamic parameters of intramolecular complex formation process of $\mathbf{1}_{a-c}$

	CHCl$_3$		Toluene	
	ΔH (kcal mol^{-1})	ΔS (cal K^{-1} mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal K^{-1} mol^{-1})
$\mathbf{1}_a$	−8.03	−24.0	5.16	18.4
$\mathbf{1}_b$	−4.87	−15.7	3.89	13.1
$\mathbf{1}_c$	−3.79	−13.8	3.34	9.6

In order to know the thermodynamic data of the intramolecular complexation process, the van't Hoff plot analysis was carried out to give the thermodynamic data (Table 2). In toluene, the entropy changes in the intramolecular complex formation are all positive, but the enthalpy changes are also positive. Apparently, the intramolecular complex formation of these C$_{60}$-linked compounds is typical entropy driven and enthalpy opposed process.

The extensive desolvation from the fullerene moiety of these compounds plays an important role in the guest inclusion process. Net positive enthalpy suggested that the energy gain due to the formation of the intramolecular complex was less than the energy loss due to the desolvation around the guest moiety (Fig. 4). In chloroform on the other hand, both the entropy and enthalpy changes in the complex formation process gave negative values in all cases. Thus, this is the typical enthalpy driven and entropy opposed process. The explanation of these data can be very similar in the case of the intermolecular complex formation in the same solvent.[8] From these analysis it is now clear that the solvation and desolvation of host and guest play a crucial role in the formation of the host–guest type supramolecular complex in solution.

References and notes

1. (a) Hirsch, A. *The Chemistry of the Fullerenes*; Thieme: Stuttgart, 1994; (b) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic: San Diego, 1996; (c) Schön, J. H.; Kloc, C.; Batlogg, B. *Nature* **2000**, *408*, 549; (d) Schön, J. H.; Kloc, C.; Batlogg, B. *Science* **2001**, *293*, 2432.
2. (a) Nakamura, E.; Isobe, H.; Tomita, N.; Sawamura, M.; Jinno, S.; Okayama, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4254; (b) Bernstein, R.; Prat, F.; Foote, C. S. *J. Am. Chem. Soc.* **1999**, *121*, 464; (c) Wada, Y.; Tsukada, M.; Fujihara, M.; Matsushige, K.; Ogawa, T.; Haga, M.; Tanaka, S. *Jpn. J. Appl. Phys.* **2000**, 3835.
3. (a) Andersson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerstrom, O. *J. Chem. Soc., Chem. Commun.* **1992**, 604; (b) Yoshida, Z.; Takekuma, H.; Takekuma, S.; Matsubara, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1597; (c) Atwood, J. L.; Koutsantnis, G. A.; Raston, C. L. *Nature* **1994**, *368*, 229; (d) Suzuki, T.; Nakashima, K.; Shinkai, S. *Chem. Lett.* **1994**, 699; (e) Atwood, J. L.; Barnes, M. J.; Bulkhalter, R. S.; Junk, P. C.; Steed, J. W.; Raston, C. L. *J. Am. Chem.*

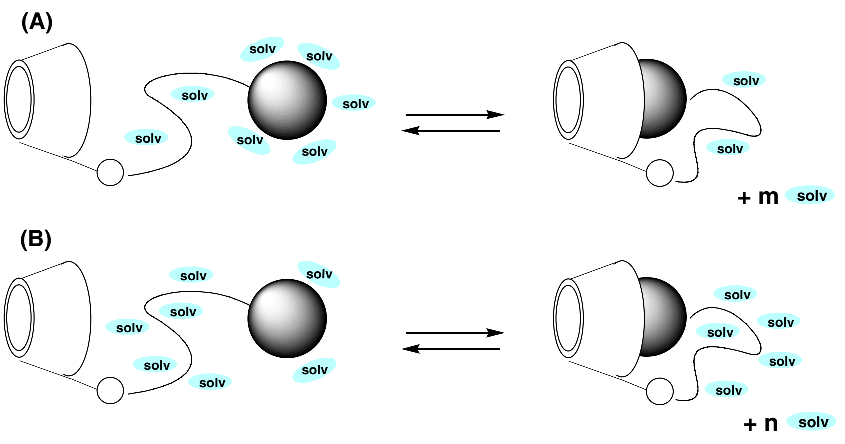


Figure 4. Schematic representation of intramolecular complexation process for **1** in each solvent (A, toluene; B, CHCl$_3$).

Soc. **1994**, *116*, 10346; (f) Matusbara, H.; Hasegawa, A.; Shiwaku, K.; Asano, K.; Uno, M.; Takahashi, S.; Yamamoto, K. *Chem. Lett.* **1998**, 923; (g) Tsubaki, K.; Tanaka, K.; Kinoshita, T.; Fuji, K. *Chem. Commun.* **1998**, 895; (h) Raston, C. L.; Atwood, J. L.; Nichols, P. J.; Sudria, I. B. N. *Chem. Commun.* **1996**, 2615.

4. (a) Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem., Int. Ed.* **1997**, *36*, 259; (b) Haino, T.; Yanase, M.; Fukazawa, Y. *Tetrahedron Lett.* **1997**, *38*, 3739; (c) Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 997; (d) Yanase, M.; Haino, T.; Fukazawa, Y. *Tetrahedron Lett.* **1999**, *40*, 2781.
5. Ikeda, A.; Nobukuni, S.; Udzu, H.; Zhong, Z.; Shinkai, S. *Eur. J. Org. Chem.* **2000**, 3287; Takeshita, M.; Suzuki, T.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2587.
6. Hawker, C. J.; Wooley, K. L.; Frechet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 925; Prato, M.; Chan Li, Q.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 1148.
7. Hawker, C. J.; Saville, P. M.; White, J. W. *J. Org. Chem.* **1994**, *59*, 3503.
8. Yanase, M.; Matsuoka, M.; Tatsumi, Y.; Suzuki, M.; Iwamoto, H.; Haino, T.; Fukazawa, Y. *Tetrahedron Lett.* **2000**, *41*, 493.