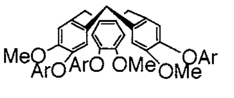
Syntheses of Novel Cyclotriveratrylenophane Capsules and Their Supramolecular Complexes of Fullerenes

Hiroshi Matsubara,* Shin-ya Oguri, Kaori Asano, and Koji Yamamoto
Department of Chemistry, College of Integrated Arts and Sciences, Osaka Prefecture University, Sakai, Osaka 599-8531

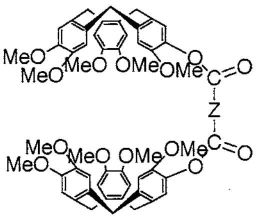
(Received February 12, 1999; CL-990093)

Cyclotriveratrylenophanes were synthesized and their inclusion abilities for fullerenes were examined by UV spectroscopy. From the spectra, the association constants were determined using Rose and Drago method. Cyclotriveratrylene hosts showed shape-selective properties and large association constants up to 19400±110 dm^3mol^{-1} for C_{60} and 26500±260 dm^3mol^{-1} for C_{70}.

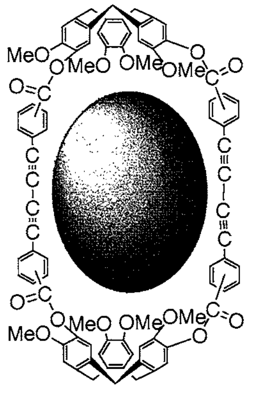
We have been interested in supramolecular inclusion abilities of cyclotriveratrylene (CTV) framework for fullerenes, and previous papers described the syntheses of CTV derivatives **1** with aromatic pendants[1] and the fullerene tweezers **2** having two CTV units.[2] An obvious extension of our interest in these studies directed our efforts to the preparation of the unique cyclotriveratrylenophane **3** with well-defined cavity sizes and their supramolecular complexes of fullerenes.



1

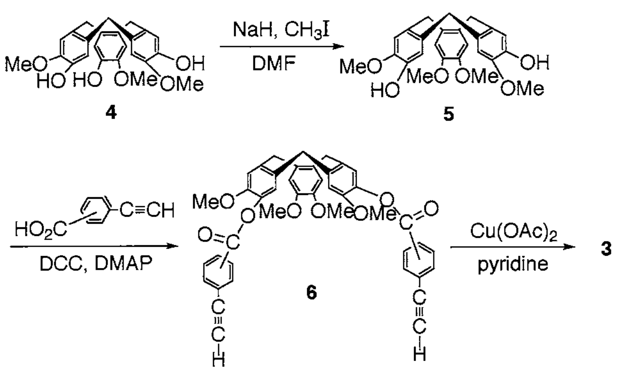


2



3a : *m*-
3b : *p*-

The synthetic pathway to the cyclotriveratrylenophane **3** is shown in Scheme 1. CTV(OH)$_3$ **4**[3] was transformed to CTV(OCH_3)$(OH)_2$ **5** (27%, mp 122-124 °C) using equimolar amount of iodomethane and NaH in DMF. Esterification of **5** with *m*- or *p*-ethynylbenzoic acid by using DCC and DMAP[4] gave bis(ethynylbenzoyl)CTV derivatives **6a** (71%, mp 138-140 °C) and **6b** (34%, mp 142-143 °C), respectively. Although the final oxidative coupling of **6** under the conditions reported by Glaser[5] or Hay[6] was unsuccessful invariably giving a recovered starting materials, high-dilution coupling (2.5 x 10^{-3} $moldm^{-3}$ of **6**) using copper acetate and pyridine at 50 °C afforded the cyclotriveratrylenophane **3a** (51%, mp 250-255 °C (dec.))[7] and **3b** (29%, mp >300 °C),[8] respectively.



Scheme 1.

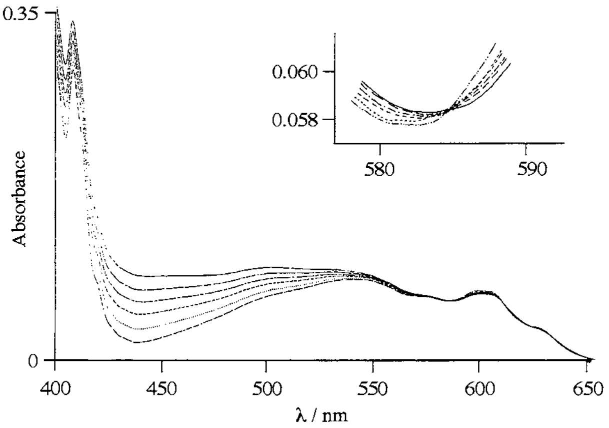


Figure 1. Absorption spectra of C_{60} (1.07 x 10^{-4} $moldm^{-3}$) in the presence of cyclotriveratrylenophane **3a** in benzene. The concentration of **3a** are from the bottom: 0.0, 0.13, 0.36, 0.58, 0.71, 0.95 (x 10^{-4} $moldm^{-3}$). Temperature : 298 K.

Immediate color change from purple to yellow was observed on mixing C_{60} and the cyclotriveratrylenophane solution. This is ascribed to the formation of host-guest complex in solution. Job's plot[9] and isosbestic point at 585 nm (Figure 1) between C_{60} and host **3**, provided evidence for a 1:1 complex in solution. The association constant of the inclusion complexes was determined from the differences of absorbance at 430-440 nm region using Rose and Drago method.[10]

Table 1. Association constants (dm^3mol^{-1}) for C_{60} at 298 K[a]

	benzene	toluene	*o*-dichlorobenzene
3a	19400±110	19100±110	10200±100
3b	6200±90	5200±90	2400±50

[a] λ=430-440 nm.

Table 1 lists the association constants of the inclusion complexes obtained by titration of **3** with C_{60} at 298 K. Although the association constants for C_{60} of CTV derivatives **1** and CTV dimers **2** prepared prevoiusly were dependent on solvents, those of cyclotriveratrylenophane **3** were almost independent on the solvents. ^{13}C NMR spectra of C_{60} were measured in the presence of the cyclotriveratrylenophane **3**.[11] Complexation-induced upfield shift $\Delta\delta$ (**3a**: 0.35, **3b**: 0.31) were observed, when the equimolar amount of C_{60} and host **3a**, **3b** were present in C_6D_6.

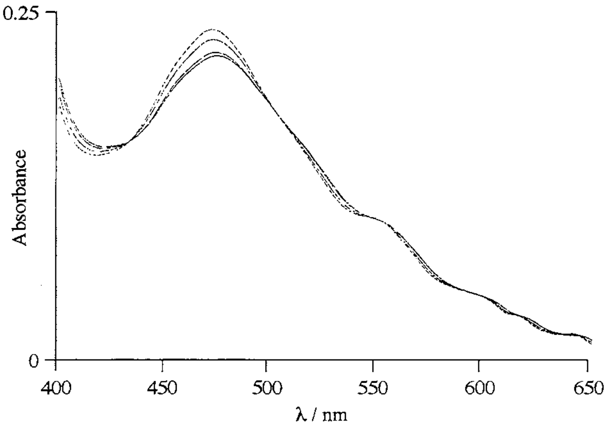


Figure 2. Absorption spectra of C_{70} (1.13×10^{-5} moldm^{-3}) in the presence of cyclotriveratrylenophane **3a** in benzene. The concentration of **3a** are from the bottom at 400 nm: 0.0, 0.11, 0.30, 0.47 ($\times 10^{-4}$ moldm^{-3}). Temperature : 298 K.

The association constants for C_{70} were also determined by the same way (Figure 2) and summarized in Table 2. Host **3** bind C_{70} preferentially to C_{60} in benzene and *o*-dichlorobenzene solution. The association constant of the complex **3a** with C_{70} has its largest value of 26500±260 dm^{3}mol^{-1} in benzene. The binding selectivity of **3b** for C_{70}/C_{60} is highest in benzene with the value of 2.5.

These observations reveal that the cyclotriveratrylenophane **3** with well defined cavity sizes (**3a**: *ca.* 11 x 15 Å, **3b**: *ca.* 11 x 17 Å, inner diameter[12]) composed of two CTV units are better suited for complexation of C_{70} than that of C_{60}.

Table 2. Association constants (dm^{3}mol^{-1}) for C_{70} at 298 K[a]

	benzene	toluene	*o*-dichlorobenzene
3a	26500±260	<300	11200±100
3b	15400±100	<300	4400±50

[a] λ=430-440 nm.

This work was partly supported by Grant-in-Aid for Scientific Research (No. 08740504) from Ministry of Education, Science, Sports, and Culture, Japan.

References and Notes

1 H. Matsubara, A. Hasegawa, K. Shiwaku, K. Asano, M. Uno, S. Takahashi, and K. Yamamoto, *Chem. Lett.*, **1998**, 923.

2 H. Matsubara, T. Shimura, A. Hasegawa, M. Semba, K. Asano, and K. Yamamoto, *Chem. Lett.*, **1998**, 1099.

3 J. Canceill, A. Collet, and G. Gottavelli, *J. Am. Chem. Soc.*, **106**, 5997 (1984).

4 B. Neises and W. Steglich, *Angew. Chem., Int. Ed. Engl.*, **17**, 522 (1978).

5 N. Darby, T. M. Cresp, and F. Sndeheimer, *J. Org. Chem.*, **42**, 1960 (1977).

6 K. Nakasuji, S. Akiyama, K. Akashi, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **43**, 3567 (1970).

7 **3a**: pale yellow powder, mp 250-255 ℃ (dec.), IR (KBr): 2200 (C≡C), 1730 (C=O), 1600 (Ar), 1500 (Ar), 1270 (C-O), 1260 (C-O), and 730 cm^{-1} (ArH), ^{1}H-NMR ($CDCl_3$): δ 3.58-3.86 (30H, m, CH_3 and CH_2), 4.77 (3H, d, J = 13.2 Hz, CH_2), 4.82 (3H, J = 15.2 Hz, CH_2), 6.79 (2H, s, ArH of CTV unit), 6.85 (2H, s, ArH of CTV unit), 6.92 (2H, s, ArH of CTV unit), 6.99 (2H, s, ArH of CTV unit), 7.12 (2H, s, ArH of CTV unit), 7.14 (2H, s, ArH of CTV unit), 7.48 (4H, m, ArH of the spacer), 7.76 (4H, m, ArH of the spacer), 8.18 (4H, m, ArH of the spacer), and 8.35 (4H, s, ArH of the spacer), MS (FAB) m/z 1352 ([M]$^+$).

8 **3b**: pale yellow powder, mp >300 ℃, IR (KBr): 2200 (C≡C), 1730 (C=O), 1600 (Ar), 1500 (Ar), 1250 (C-O), and 850 cm^{-1} (ArH), ^{1}H-NMR ($CDCl_3$): δ 3.65 (6H, d, J = 14.1 Hz, CH_2), 3.78-3.86 (24H, m, CH_3), 4.84 (6H, d, J = 14.1 Hz, CH_2), 6.82 (2H, s, ArH of CTV unit), 6.86 (2H, s, ArH of CTV unit), 6.92 (2H, s, ArH of CTV unit), 6.99 (2H, s, ArH of CTV unit), 7.15 (2H, s, ArH of CTV unit), 7.20 (2H, s, ArH of CTV unit), 7.64 (8H, d, J = 8.3 Hz, ArH of the spacer), and 8.15 (8H, m, ArH of the spacer), MS (FAB) m/z 1352 ([M]$^+$).

9 U. M. Rabie, B. P. Patal, and R. H. Crabtree, *Inorg. Chem.*, **36**, 2236 (1996); S. C. Zimmerman, W. Wu, and Z. Zeng, *J. Am. Chem. Soc.*, **113**, 196 (1991).

10 N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

11 We also measured ^{1}H NMR spectra of the host **3** in the presence of C_{60} or C_{70} in C_6D_6, however, little upfield shifts were observed among these spectra ($\Delta\delta$ < 0.1ppm).

12 Using Corey-Pauling-Kolton (CPK) space-filling molecular models.