Supramolecular Inclusion Complexes of Fullerenes Using Cyclotriveratrylene Derivatives with Aromatic Pendants

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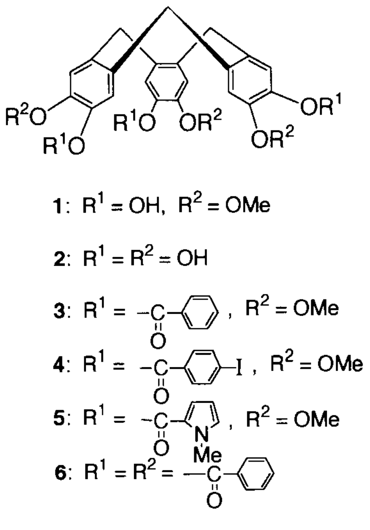
CTV derivatives with aromatic pendants were synthesized and their inclusion abilities for C_{60} and C_{70} were examined by UV spectroscopy. CTV derivative with three N-methylpyrrole pendants showed the highest association constant for C_{60} (48000 dm^3mol^{-1} in benzene). The structure of inclusion complex for C_{60} with CTV derivative which has six benzoyl pendants has been determined by single-crystal X-ray diffraction.

Recently there are considerable attention and development of supramolecular complexes between fullerenes and macrocycles, such as calixarene,[1] cyclotriveratrylene (CTV),[2] and γ-cyclodextrin.[3] Despite these large amount of research, however, it is surprising that few studies have led to excellent complexation for fullerenes in organic solution, except for recent publication of supramolecular complex of C_{60} using homooxacalix[3]arene[4] and calix[n]arene (n = 5, 6).[5] From the attractive studies for selective formation of a clathrate from CTV and C_{60} in a solution,[6] we directed our efforts to synthesis of four types of CTV derivatives having various aromatic pendants which should display efficient inclusion ability towards fullerenes.

In this paper, we wish to report the inclusion abilities of CTV derivatives **3**, **4**, **5**, and **6** for fullerenes in organic solvents and the successful X-ray crystallographic analysis of the supramolecular inclusion complex of **6** for C_{60}.

Esterification of $CTV(OH)_3$ **1**[7] with various acyl chlorides in the presence of pyridine provided the CTV derivatives **3** and **4**, whereas host **5** which has N-methylpyrrole pendants was prepared by reaction of **1** with N-methylpyrrole-2-carboxylic acid in the presence of DCC and DMAP because of liability of a pyrrole ring in acid conditions. The host **6** with six benzoyl pendants was also prepared in the same way using $CTV(OH)_6$ **2**[8] and benzoyl chloride in the presence of pyridine.

A color change from violet to light yellow was observed on mixing C_{60} and CTV derivatives **3**-**6** solution. This indicates formation of host-guest complex in solution. Examination of a Job's plot[9] between the host **3**-**6** and C_{60} (the concentration of the host is the range 0.1 eq. to 1.0 eq. for C_{60}) provided the monotonous increasing carve with the highest value at 1.0 eq. for C_{60}, however, presence of the host more than 1.0 eq. for C_{60} showed large deviation from normal behavior because of a separation of brown precipitation analyzing as the host:C_{60} = 2:1 complex.[10] This phenomenon seems to be indicate that a Job's plot provided evidence for host:C_{60} = 1:1 complex under the mixing conditions of C_{60} and the CTV derivatives (≤ 1.0 eq.) solution.



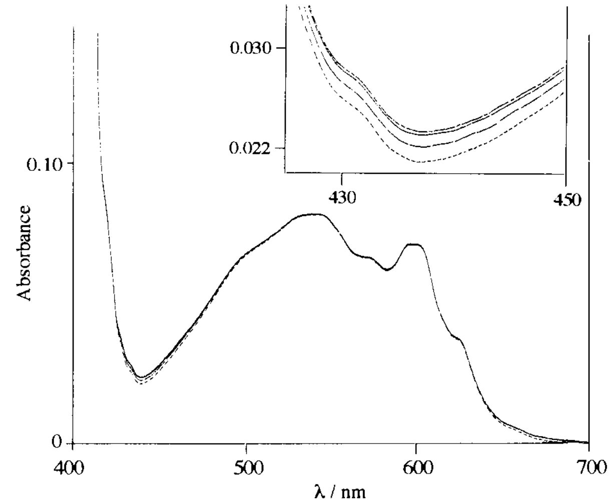


Figure 1. Absorption spectra of C_{60} (1.06 × 10^{-4} $moldm^{-3}$) in the presence of CTV derivative **5** in benzene. The concentration of **5** are from the bottom: 0.0, 0.19, 0.41, 0.75 (× 10^{-4} $moldm^{-3}$). Temperature : 298 K.

Addition of the host to a solution of C_{60}, its UV spectrum was changed continuously with some isosbestic points and the intensity at 430-440 nm region increased (Figure 1). Titration of the CTV derivatives were also carried out in the range of 0.1 eq. to 0.8 eq. for C_{60}. The association constants (Table 1) of the inclusion complexes were determined using modified Benesi-Hildebrand method[11] confirmed a 1:1 stoichiometry for the host-guest complexes. CTV derivatives synthesized here showed considerable large association constants. Especially, host **5** which has N-methylpyrrole pendants exhibited quite large association constants (48000 dm^3mol^{-1}, in benzene). The association constants of C_{70} were also determined by the same way and summarized in Table 1. Among CTV derivatives prepared here, host **4** and **5** showed inclusion ability for C_{70}. It

Table 1. Association constants (dm^3mol^{-1}) for CTV derivatives **3**-**6** with fullerenes at 298K[a]

	C_{60}		C_{70}	
	benzene	toluene	benzene	toluene
3	9000±130	5500±80	0	0
4	7800±50	——[b]	16800±130	——[b]
5	48000±250	36300±300	7700±200	13900±80
6	4000±30	13000±60	0	0

[a] λ = 430-440 nm. [b] not determined yet, bacause inclusion complex was precipitated immediately.

is particularly interesting that host **4** with *p*-iodobenzoyl pendants exhibited a larger association constant for C_{70} than that for C_{60}.

Slow concentration of a solution of an excess of the host **3**-**6** and C_{60} afforded the precipitated inclusion complexes. Although most inclusion complexes gave fine needles, $CTV(OBz)_6$ **6** and C_{60} in toluene provided dark brown prisms suitable for X-ray crystallographic analysis. In order to suppress thermal vibration and/or rotation of C_{60} in the molecules X-ray analysis[12] was carried out at −120 °C. The crystal packing for the molecule was displayed in Figure 2. It is very interesting that there were two kind of C_{60}, one is encapsulated within a cavity of the two host molecules, the other is located without hosts between two "included C_{60}". The included C_{60} and the bare C_{60} were located at body-centered lattice and the side of the lattice, respectively. The inclusion complexes existed roughly in the *bc* plane, and both kind of C_{60} were stacking orderly along *a*-axis. There were 42 interatomic distances shorter than 3.8 Å between the sp^2 carbons in the included C_{60} and two hosts, which indicates a strong association formed in the inclusion complex.

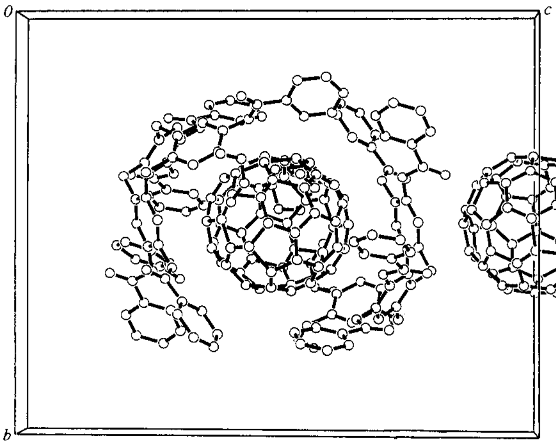


Figure 2. Crystal packing of the inclusion complex for C_{60} with host **6** along *a*-axis. Only the included C_{60} with two of the hosts and the bare C_{60} are shown.

Finally, we examined the convenient purification[13] of C_{60} from fullerite (C_{60} and C_{70} mixture) using CTV derivative **3** which selectively forms a complex for C_{60}.

Excess the host **3** was added to a toluene solution of fullerite and warmed at 50 °C for 30 min. After cooling, filtration of the resulting complex followed by washing with toluene and acetonitrile gave a pure C_{60} powder whose purity was determined by HPLC analysis.[14] The host and C_{70} were also recovered from the organic solution.

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10 For example, in the case of host **3** and C_{60}. Calcd for $[CTV(OBz)_3]_2 \cdot C_{60}$, $C_{150}H_{72}O_{18}$: C, 83.32; H, 3.36; O, 13.32%. Found: C, 83.11; H, 3.34%.

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12 Crystal data of the inclusion complex (instrument: Rigaku RAXIS-IV imaging plate area detector): **6** $(C_{63}H_{42}O_{12}) \cdot C_{60} \cdot (\text{toluene})_{1.5}$, FW = 1848.38, 0.2 × 0.2 × 0.2 mm, monoclinic, $P2_1/n$ (#14), a = 15.5669(3) Å, b = 21.0311(4) Å, c = 26.1924(6) Å, β = 101.6121(5)°, V = 8399.6(3) $Å^3$, Z = 4, D_{mesure} = 1.403 g/cm^3, D_{calc} = 1.462 g/cm^3, μ (Mo, Kα) = 0.93 cm^{-1}, temperature -120 °C, R = 0.128, R_w = 0.114, GOF = 0.600 for 10676 independent reflections ($I > 2.00\sigma(I)$). A few carbon atoms of the included C_{60} were disorded.

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14 HPLC conditions: column, COSMOSIL $5C_{18}$; mobile phase, toluene : methanol = 1:1 v/v; λ = 340 nm.