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A Self-Assembling Molecular Container for Fullerenes

Manabu Yanase, Takeharu Haino, and Yoshimasa Fukazawa*

Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima City 739-8526 Japan

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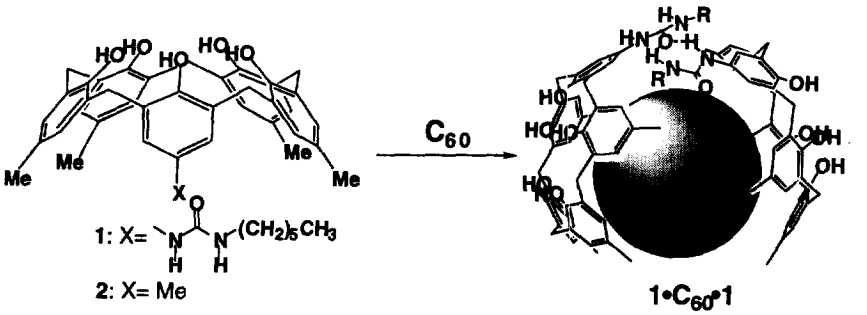
Abstract: Encapsulation of C_{60} by a self-assembled supramolecular capsule based on a calix[5]arene urea derivative is described. Release of the entrapped fullerene from the ternary complex can be easily managed by the addition of a protic acid. Two pathways to give the supramolecular ternary complex are analyzed successfully.

Molecular capsules composed of self-assembling bowl-shaped molecules are of particular interest[1] because these capsules can control both binding and release of guest molecules.[2] Non-covalent forces lead to the assembly of small subunits into large superstructures. Polar functional groups such as urea and amide play an important role in assembling subunits with hydrogen bondings.[3] Calixarenes having such polar functional groups on the upper-rim were reported to form spherical self-assembling capsule in which small organic molecules were encapsulated.[4] However, although extensive studies of complexation of C_{60} with various hosts have been reported,[5] non of self-assembling molecular capsule capable of binding fullerenes is known. Recently, we have reported that calix[5]arenes gave supramolecular complexes with C_{60} both in solution and in the crystalline state.[6] In the crystalline complex with the stoichiometry of 2 : 1 (host : guest), the guest was fully encapsulated within the two calix[5]arenes.[7] The structural integrity of this crystalline complex, however, is not high enough and



when dissolved in organic solvent it decomposed to a 1 : 1 complex with one molecule of the host liberated. Increasing the stability of the 2 : 1 complex was achieved by connecting the two hosts with suitable linkages.[8] However, as a result of the linkages the guest is encapsulated strongly within the bicapped host and the separation of the guest from the complex is rather difficult. Hence, we have designed a self-assembling molecular capsule capable of both binding and release of fullerenes in solution.

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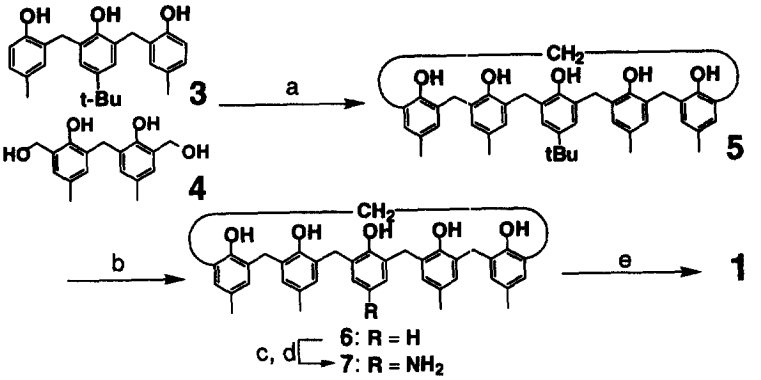
Calix[5]arene **1** bearing urea functionality is designed. The cavity formed by two calix[5]arenes is large enough to give a supramolecular complex with C_{60}. Dissociation of the self-associated **1**• **1** complex can be achieved with cleavage of hydrogen bonds by the addition of excess amount of other hydrogen bond donor or acceptor. In this paper we report a synthesis and binding behavior of **1** with C_{60}. Synthesis of **1** is shown in Scheme. Simple heating of **3** and **4** in refluxing xylene[9] gave the condensation product **5**. Debutylation of **5** with $AlCl_3$ in the presence of excess amount of phenol gave **6**. Diazo coupling of **6**, followed by reductive cleavage of N=N double bond furnished amino calix[5]arene **7**. Treatment of **7** with n-hexyl isocyanate afforded the desired host molecule **1**.



Scheme. a) xylene, Δ (19%); b) phenol, $AlCl_3$/ toluene (82%);
c) *p*-aminobenzoicacid, $NaNO_2$, 6N-HCl / H_2O, and then CH_3COONa/ MeOH-DMF
d) $Na_2S_2O_4$, 1% NaOHaq. (65%); e) n-Hexyl Isocyanate/ CH_2Cl_2 (25%).

The self association of **1** was investigated with ^{1}H-NMR by variation of the concentration of **1** in $CDCl_3$-CS_2(2:1 v/v). N-H proton signals shifted to the down-field as the concentration of **1** was increased from 7.4×10^{-5} to 5.9×10^{-3} dm^3/mol. The titration curve indicated the formation of a self-assembled dimer **1**• **1**. The formation constant of the dimer was determined by a non-linear least squares curve fitting program to be 32 (3) dm^3/mol.[10] In the presence of a small amount of C_{60} (9.4×10^{-4} dm^3/mol) it increased significantly (Ka = 104 (7) dm^3/mol), indicating the formation of a ternary complex **1**• C_{60}• **1**. Similar increase of the association constant was also observed in the presence of a small amount of C_{70}.

The formation of the ternary complex was further confirmed by the complexation induced shift of ^{13}C-NMR signal of C_{60}. The ^{13}C signal of C_{60} was shifted to the up-field when added a solution of **1**. In the presence of the excess amount of the host, the complexation induced up-field shift value of C_{60} is 0.82 ppm (the concentrations of C_{60} and **1** are 9.2×10^{-4} and 3.7×10^{-3} dm^3/mol, respectively.) It decreased to 0.21 ppm when an excess amount of trifluoroacetic acid (2 times of **1**) was added into the solution. Similar up-field shift of the guest was observed in the presence of an excess amount of a non self-assembling host **2**. However, the complexation induced up-field shift did not change at all even after the addition of a large amount of trifluoroacetic acid. The result indicated that the ternary complex dissociated by the protonation of urea group to increase the concentration of the free guest. Thus the addition of the acid inhibits the self-association of the host, and promotes the liberation of the encapsulated guest.

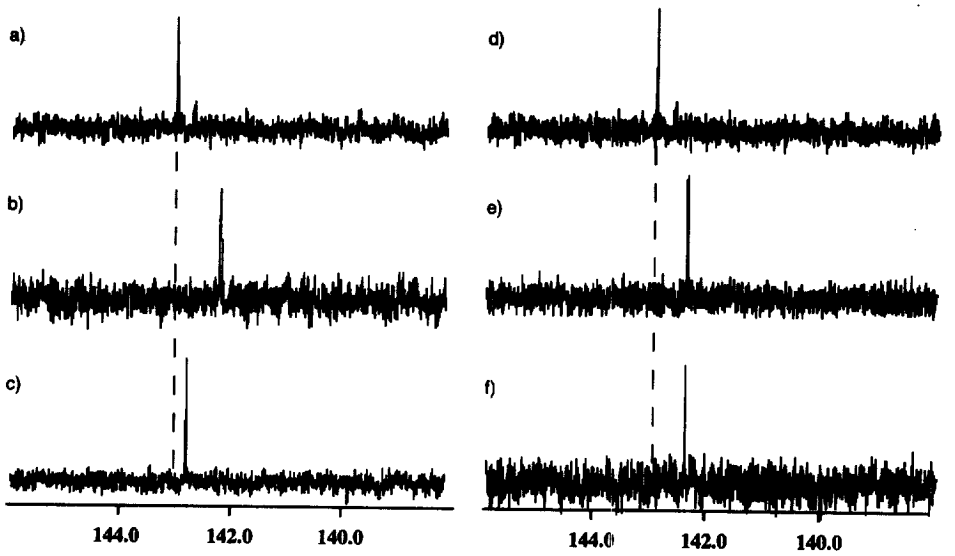


Figure 1. Complexation induced shifts of C_{60} .

(a) C_{60} ($9.2x10^{-4}M^{-1}$) in $CHCl_3$-CS_2(2:1 v/v); (b) C_{60} ($9.2X10^{-4}M^{-1}$) in $CHCl_3$-CS_2(2:1 v/v) with 4 equivalents of **1** added; (c) C_{60} ($9.2X10^{-4}M^{-1}$) in $CHCl_3$-CS_2(2:1 v/v) with 4 equivalents of **1** and 2 equvalents of TFA added ; (d) C_{60} ($4.6X10^{-4}M^{-1}$) in $CHCl_3$-CS_2(2:1 v/v); (e) C_{60} ($4.6X10^{-4}M^{-1}$) in $CHCl_3$-CS_2(2:1 v/v) with 5 equivalents of **2** added; (f) C_{60} ($4.6X10^{-4}M^{-1}$) in $CHCl_3$-CS_2(2:1 v/v) with 5 equivalents of **2** and 2 equivalents of TFA added.

There are two pathways to give the ternary complex; one is the sequential stepwise formation via 1:1 host guest complex and the other is direct encapsulation of the guest within the vacant **1**• **1** dimer. In order to analyze the former pathway a titration study was carried out in a mixed solvent system, $CDCl_3$-CS_2 (2:1 v/v), using variations of the complexation induced ^{13}C-NMR chemical shifts of the guest vs. concentrations of **1**. The association constants, determined by a non-linear least squares curve fitting program using Simplex algorithm,[11] were 450 and 110 dm^3/mol for the first and second step, respectively.[10] Although the formation constant of the second pathway, the direct encapsulation into the vacant **1**• **1**, was not obtained by any experiment it can be easily estimated from the association constants

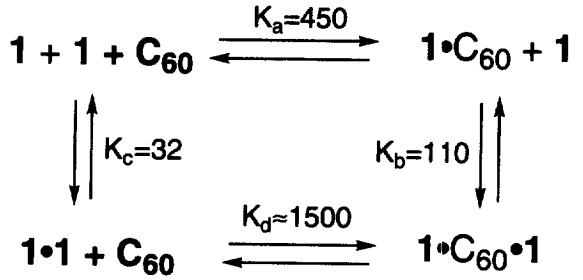


Figure 2. Schematic presentation of the association processes and association constants (dm^3/mol).

for the two steps. The value (ca. 1500 dm^3/mol) is nearly identical to the association constant of the ethynyl bridged double calix[5]arene with C_{60} in CS_2 (1500 (100) dm^3/mol).[8] Since the values obtained for the association constants of the two sequential steps by the single titration curve is not as accurate as that of the single process, the close similarity of the two association constants gave another support of the reliability of the analysis. Easy control of both binding and release of the fullerenes with self-assembling host can be a new method for a direct purification of fullerenes.

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