Inclusion of [60]Fullerene in a Homooxacalix[3]arene-Based Dimeric Capsule Cross-Linked by a Pd(II)−Pyridine Interaction

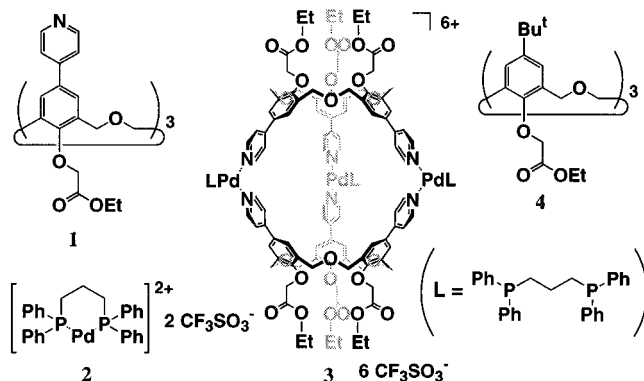Atsushi Ikeda, Makoto Yoshimura, Hiromi Udzu, Chie Fukuhara, and Seiji Shinkai*

Department of Chemistry & Biochemistry
Graduate School of Engineering
Kyushu University, Fukuoka 812-8581, Japan

In 1994, we[1] and Atwood et al.[2] discovered that *p-tert*-butylcalix[8]arene selectively includes [60]fullerene in carbon soot and forms the precipitate with 1:1 stoichiometry. This is a very novel and very useful purification method to obtain [60]fullerene in large quantity and with high purity.[1−4] More recently, it was shown that certain calix[*n*]arenes and their analogues can interact with [60]fullerene even in solution.[5−13] The X-ray structure of a [60]fullerene·calix[5]arene complex showed that [60]fullerene is included in a cavity composed of two calix[5]arene half-bowls.[8] This picture stimulated us to design such a dimeric capsule molecule composed of two calix[*n*]arenes for inclusion of [60]fullerene.[14] Here, it occurred to us that the utilization of a coordination bond for this purpose has been a hitherto missed opportunity, for Fujita et al.[15] and Stang et al.[16] have shown a number of examples where the coordination bond is very useful for the construction of self-assembling supramolecular structures. We thus designed compound **3**; the ^{1}H NMR and mass spectroscopic studies and

VPO measurements showed that two homooxacalix[3]arenes (**1**) dimerize in the presence of 3 equiv of Pd(II)(Ph₂PCH₂CH₂CH₂-PPh₂)·(OTf⁻)₂ (**2**) into a molecular capsule (**3**).[17]

As shown in Figure 1A, a 2:3 **1**/**2** mixture gave a ^{1}H NMR spectrum assignable to **3** with a D_{3h}-symmetrical structure.[17] The guest molecules tested herein were DMF, DMSO, nitromethane, adamantane, 1,2,4,5-tetramethylbenzene, anthracene, pyrene, sodium picrate, and others. However, none of these compounds could give the separate NMR peaks or induce the chemical shift change attributable to the host·guest complex formation. Examination of the CPK molecular models reveals that three windows in **3** are large enough to allow permeation of these guest molecules. Only when ^{13}C-enriched [60]fullerene (^{13}C content ca. 12%) was added,[18] did new peaks appear in both the ^{1}H and ^{13}C NMR spectra.

In the ^{13}C NMR spectrum (Figure 2), a new peak appeared at higher magnetic field (140.97 ppm) than the peak for free **3** (142.87 ppm). This peak is assignable to the **3**·[60]fullerene inclusion complex, and the peak separation implies that the complexation−decomplexation exchange rate is slower than the ^{13}C NMR time scale.[19] According to Cram's studies on molecular containers,[20] the rate of the guest liberation from a hemicarcerand is related not only to the size of the guest molecules but also to the rigidity and the shape. [60]Fullerene is exactly classified into such a rigid and spherical guest, and therefore, the exchange rate can be slower than the ^{13}C NMR time scale. In the presence of **1** (instead of **3**) the ^{13}C NMR spectrum of [60]fullerene was scarcely changed. The result is consistent with our previous finding that the ethoxycarbonylmethyl derivatives of homooxacalix[3]arene cannot interact with [60]fullerene in the absence of alkali metal cations.[6] When **2** was added, the [60]fullerene peak shifted by 0.07 ppm to a higher magnetic field. It is known that Pd⁰ can coordinate to [60]fullerene to form the η-complexes,[21] but to the best of our knowledge there is no clear evidence for the interaction between Pd(II) and [60]fullerene in organic solvents.[22] The slight chemical shift change induced by **2** suggests that a weak and rapidly exchangeable interaction may be operative between **2** and [60]fullerene.

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(18) The solutions for the ^{1}H and ^{13}C NMR spectral measurements were prepared as follows: the Cl₂CDCDCl₂ solution of **3** (5.0 mmol dm⁻³: 0.1 dm³) was mixed with the Cl₂CDCDCl₂ solution of [60]fullerene (5.9 or 0.59 mmol dm⁻³: 0.9 dm³), and the mixture was sonicated for 6 h.
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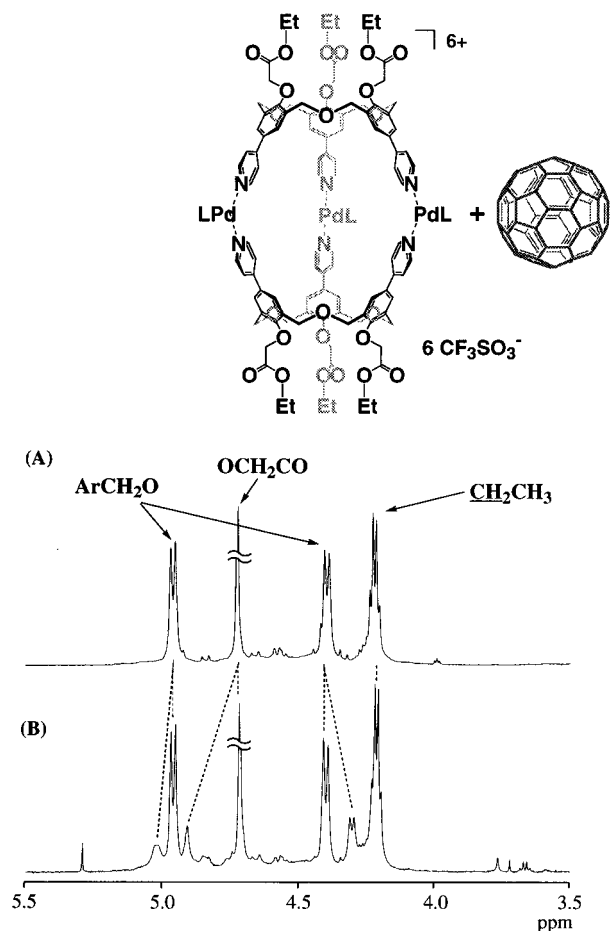
Scheme 1

Figure 1. Partial ^{1}H NMR spectra of (A) [**1**]:[**2**] = 2:3 (1.0 mmol dm^{-3}:1.5 mmol dm^{-3}) and (B) [**3**] (0.50 mmol dm^{-3}) in the presence of [60]fullerene (5.3 mmol dm^{-3}): 600 MHz, Cl$_2$CDCDCl$_2$, 60 °C.
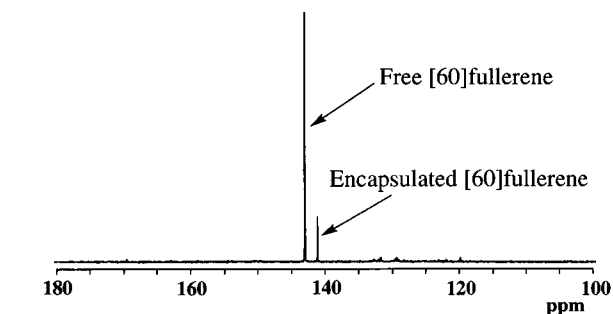

Figure 2. Partial ^{13}C NMR spectrum of ^{13}C-enriched [60]fullerene (0.5 mmol dm^{-3}) in the presence of **3** (0.5 mmol dm^{-3}): 150 MHz, Cl$_2$CDCDCl$_2$, 25 °C.

The ^{1}H NMR spectrum of **3** in the presence of [60]fullerene is shown in Figure 1B.[18] In Figure 1B, the proton signals for free **3** and those for the **3**·[60]fullerene complex appeared separately, and these signals were not coalesced even at 90 °C. At 60 °C the assignment (Figure 3) was successfully attained using the ^{1}H$-$^{1}H COSY spectrum. It is known that the angle of the phenyl units with respect to the calixarene ring plane can be estimated by the chemical shift difference ($\Delta\delta_H$) between axial and equatorial protons in the ArCH$_2$O methylene groups.[6,23] In the absence of [60]-fullerene the $\Delta\delta_H$ of **3** was 0.56 ppm. This value is close to that of **4** (0.48 ppm, 30 °C, toluene-d_8:CD$_3$OD = 44:1 v/v). In contrast, the $\Delta\delta_H$ of the **3**·[60]fullerene complex was increased to 0.72 ppm, which is similar to that of the **4**·Li$^+$ complex (0.68 ppm, 30 °C, toluene-d_8:CD$_3$OD = 44:1 v/v) which has flattened phenyl groups to include [60]fullerene in the cavity.[6] These results

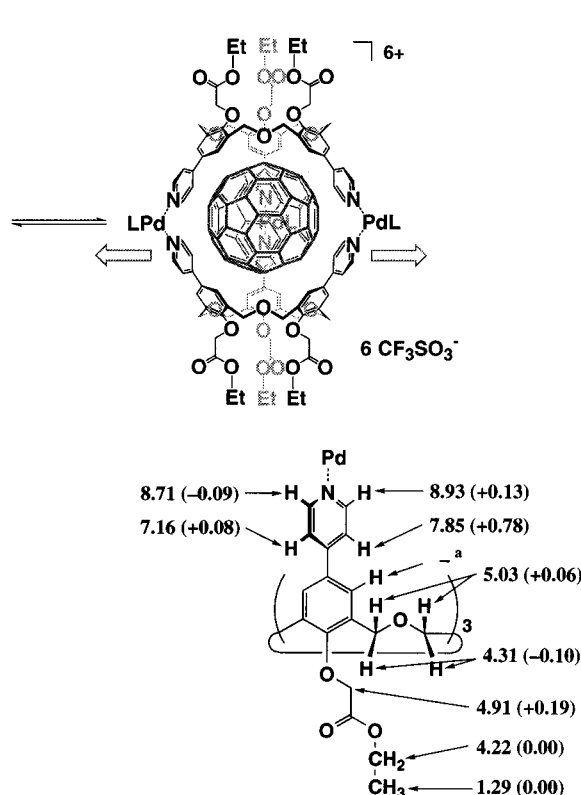**Figure 3.** Assignment of the **3**·[60]fullerene complex. The numbers indicate the chemical shifts ($\Delta\delta_H$): 600 MHz, Cl$_2$CDCDCl$_2$, 60 °C, [**3**] = 0.50 mmol dm^{-3}, [[60]fullerene] = 5.3 mmol dm^{-3}. The numbers in parentheses denote the shift from uncomplexed **3** (+ to lower magnetic field, − to higher magnetic field). ^{a}The chemical shift of the ArH protons of calixarene overlaps with those of other aromatic protons.

indicate that to interact with [60]fullerene, the phenyl groups in **3** must be also flattened to create a cavity shape suitable for inclusion of [60]fullerene (Scheme 1). The simple signals observed for the **3**·[60]fullerene complex imply that, even after including [60]fullerene, **3** maintains a D_{3h}-symmetrical structure. The α- and β-pyridyl proton signals for the **3**·[60]fullerene complex appeared separately, indicating that the rotation of the pyridine moieties becomes slower than the ^{1}H NMR time scale.[24] The change in the rotational speed is ascribed to "steric hindrance" of included [60]fullerene. The large downfield shift observed for one α- and one β-pyridyl proton (+0.13 ppm and +0.78 ppm, respectively) suggests that these protons are affected by the π-electron ring current of the included [60]fullerene. The association constant (K_{ass}) could be readily estimated from the ratio of the peak intensity of free **3** and the **3**·[60]fullerene complex to be 54 dm^3 mol^{-1}.

In conclusion, the present paper demonstrates the first example for the inclusion of [60]fullerene in a capsule-like cage molecule. The cage molecule can disrupt [60]fullerene−solvent, [60]fuller-ene−[60]fullerene interactions, so that (i) one may estimate "uni-molecular" chemical and physical properties of [60]fullerene in polar solvents, (ii) one may inhibit undesired photodimerization of [60]fullerene, or (iii) only the specific substrate which can pass through the window of the cage molecule may react with [60]-fullerene.

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