Host–Guest Chemistry

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Size-Selective Encapsulation of C_{60} by [10]Cycloparaphenylene: Formation of the Shortest Fullerene-Peapod**

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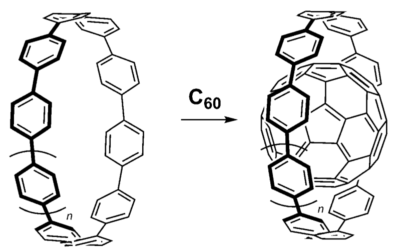

Figure 1. Structures of cycloparaphenylene (CPP) and C_{60} encapsulated CPP.

Cycloparaphenylenes (CPPs) are hoop-shaped π-conjugated molecules in which paraphenylene units are linked in a cyclic manner (Figure 1). They represent the simplest structural unit of armchair carbon nanotubes. Owing to their unique structures, CPPs have attracted the attention of theoretical, synthetic, and supramolecular chemists for more than half a century.[1–6] Based on the analogy to layered carbon networks with curved surfaces, for example multiwalled carbon nanotubes,[7,8] bucky onions,[9,10] and fullerene-peapods,[11–13] the concave cavity of the CPPs should act as a host for π-conjugated molecules with a convex surface, such as fullerenes. Such a host–guest complex would be a suitable model for elucidating convex–concave π–π interactions.[4,14–16] Although Kawase et al. have reported the complexation of cycloparaphenyleneacetylenes with fullerenes,[17–21] there have been no reports of the formation of host–guest complexes with CPPs so far. During studies on the synthesis of CPPs[22–24] by our own approach[25] and elucidation of their properties,[26,27] we found the first example of a host–guest complex of CPP and C_{60}.[28] Here we report the size-selective encapsulation of C_{60} by [10]CPP, which represents the shortest fullerene-peapod.

The size-selective interaction between a CPP and C_{60} was observed by ^{1}H NMR spectroscopy when an excess amount of solid C_{60} was added to a mixture of [8]-, [9]-, [10]-, [11]-, and [12]CPPs in $CDCl_3$. The ^{1}H NMR signal for [10]CPP shifted downfield by roughly 0.054 ppm, whereas the other signals did not change (Figure 2a). The same downfield shift was observed when C_{60} was added to a solution of isolated [10]CPP (Figure 2b). The interaction was also confirmed by ^{13}C NMR spectroscopy: the C_{60} signals shifted upfield by approximately 1.4 ppm and the *ipso* carbon of [10]CPP shifted by about 0.3 ppm, while the chemical shift of the *ortho* carbon of [10]CPP did not change significantly (<0.1 ppm).[29,30] Since the ^{1}H NMR resonance of [6]cycloparaphenyleneacetylene also shifted downfield upon encapsulation of C_{60},[18] the result indicated that [10]CPP selectively encapsulated C_{60} forming [10]CPP$\supset C_{60}$.

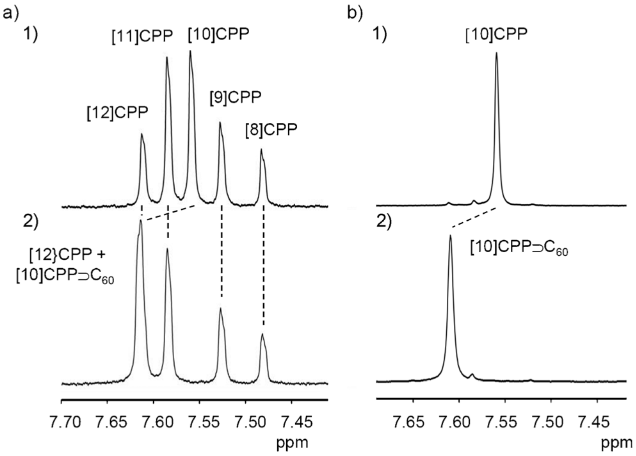

Figure 2. ^{1}H NMR spectra in $CDCl_3$ at room temperature of a) [8]–[12]CPPs before (1) and after (2) the addition of C_{60} and b) isolated [10]CPP before (1) and after (2) the addition of C_{60}.

The formation of a 1:1 complex between [10]CPP and C_{60} was first suggested by UV/Vis titration (see the Supporting Information). A Job's plot monitored at 420 nm in toluene showed a maximum absorption change when the ratio of [10]CPP and C_{60} reached 1:1.[31] In addition, an isosbestic point at 512 nm was observed in 1,2-dichlorobenzene, which is a better solvent for C_{60} than toluene. The binding constant K_a in 1,2-dichlorobenzene was determined to be $(6.0 \pm 0.2) \times 10^3\,L^{-1}$mol, a value smaller than that obtained in toluene (see below).[32] In atmospheric-pressure chemical-ionization

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time-of-flight (APCI TOF) mass spectrometry in negative-ion mode, a molecular ion peak corresponding to a 1:1 complex (*m*/*z* 1481.316) was observed.

C_{60} quenched the fluorescence of [10]CPP (Figure 3). The Stern–Völmer constant (K_{SV}) and binding constant (K_a) in toluene were determined by fluorescence-quenching experiments[33,34] to be $(4.34 \pm 0.04) \times 10^6\,L^{-1}$mol and $(2.79 \pm 0.03) \times 10^6\,L^{-1}$mol, respectively. The results revealed that [10]CPP and C_{60} are stabilized about 38 kJ mol^{-1} by the encapsulation.[35,36] The values are about 100 times larger than those obtained for [6]cycloparaphenyleneacetylene$\supset C_{60}$ and very similar to those for [6](1,4)naphthyleneacetylene$\supset C_{60}$,[4,17] which is the strongest host reported so far for C_{60} consisting of simple hydrocarbons.

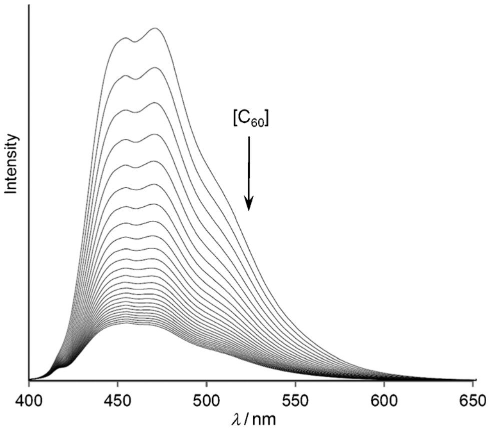

Figure 3. Fluorescence spectra of [10]CPP (5.13×10^{-7} mol L^{-1}, $\lambda_{exc} = 370$ nm) in the presence of C_{60} in toluene. The concentrations of C_{60} are 0.0–12.30 ($\times 10^{-7}$ mol L^{-1}) from the top to the bottom.

Variable-temperature NMR spectroscopy was carried out to observe the dynamics of the complexation (Figure 4). In the spectra of a 2:1 mixture of [10]CPP and C_{60} in CD_2Cl_2, a sharp singlet at 7.61 ppm was observed at room temperature. The result indicates the rapid exchange between free [10]CPP and [10]CPP$\supset C_{60}$ at room temperature. Two singlets corresponding to free [10]CPP and [10]CPP$\supset C_{60}$ were observed at 7.48 and 7.51 ppm at −80 °C. Although the signals showed different temperature dependency, they coalesced at (-5 ± 2.5) °C. The Gibbs activation energy for the exchange reaction between [10]CPP and [10]CPP$\supset C_{60}$ was determined to be (59 ± 1) kJ mol^{-1} in CD_2Cl_2.

The encapsulation of C_{60} by [10]CPP was further examined by DFT calculations at the M06-2X/6-31G* level of theory (Figure 5).[37] Complex formation is highly exothermic with a calculated heat of formation (ΔH) of 173 kJ mol^{-1}. While the calculation overestimated the stabilization energy, a strong attractive interaction between [10]CPP and C_{60} is suggested. In the most stable conformation, C_{60} sits inside the cavity of [10]CPP. The dihedral angles between two adjacent paraphenylene units of [10]CPP$\supset C_{60}$ are between 26° and 28°—significantly smaller than the dihedral angles of free [10]CPP (32–33°).[27,38,39] However, since a singlet signal was observed in the ^{1}H NMR spectrum of [10]CPP$\supset C_{60}$ even at low temperature, the paraphenylene unit in the complex must be structurally flexible and be rapidly fluttering at this temperature.

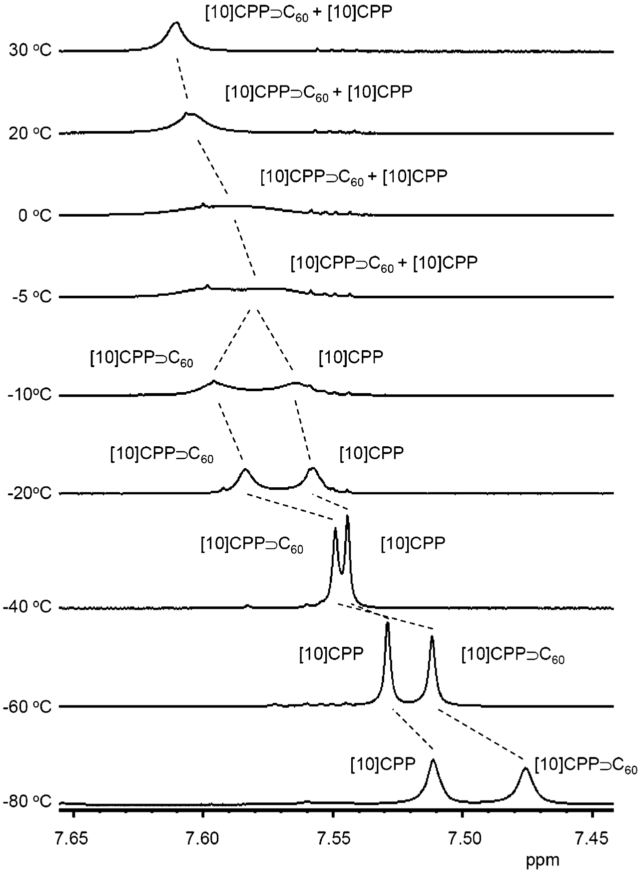

Figure 4. Variable-temperature ^{1}H NMR spectra of a 2:1 mixture of [10]CPP and C_{60} in CD_2Cl_2.

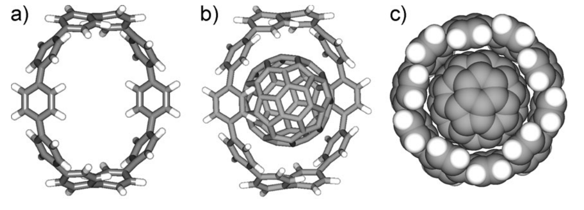

Figure 5. Structure of a) [10]CPP, b) [10]CPP$\supset C_{60}$ complex (side view), and c) its space-filling model (top view) optimized at the M06-2X/6-31G* level of theory.

A space-filling model of the complex indicates that the space inside the cavity of [10]CPP is almost completely filled by C_{60} (Figure 4c). The diameter of [10]CPP (1.38 nm[27]) is 0.67 nm larger than that of C_{60} (0.71 nm). The distance between C_{60} and [10]CPP (0.335 nm) coincides with the interplanar van der Waals distance between graphite sheets.[40] This interlayer distance has been also observed in π materials possessing convex–concave interactions, such as multiwalled carbon nanotubes,[8] fullerene peapods,[11] and [6]cycloparaphenyleneacetylene$\supset C_{60}$.[4,18]

The diameters of [9]- and [11]CPPs are 1.24 and 1.52 nm, respectively, and their cavity sizes are not appropriate for forming a strong complex with C_{60}. The DFT calculations suggest that the encapsulation of C_{60} by [9]CPP and [10]CPPs are exothermic with $\Delta H = 110$ and $111\ \mathrm{kJ\,mol^{-1}}$, respectively,[41] and these values are roughly $60\ \mathrm{kJ\,mol^{-1}}$ lower than that calculated with [10]CPP. Since the calculation at the M06-2X level considerably overestimates interactions between CPP and C_{60} as suggested above, the absolute values are unreliable. However, the relative stabilities of the complexes should be highly reliable. Therefore, the results indicate that the encapsulation by [9]- and [11]CPPs is far less attractive than that by [10]CPP, and that the size of CPP is important for maximizing concave–convex π–π interactions.

In summary, C_{60} was selectively encapsulated by [10]CPP. This finding opens the possibility of utilizing CPPs as size- and shape-selective host molecules for various guest molecules. Since several CPPs with different sizes are now available,[22–27] they would also serve as selective hosts for certain fullerenes[42] and even carbon nanotubes depending on their size. Such complementary host–guest chemistry will be useful for the size- and shape-selective separation of higher fullerenes and carbon nanotubes.[43–47]

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[33] Data were fitted by using the following equation:[34] $F/F_0 = (1+(k_f/k_s)K[\mathrm{L}])/(1+K_a[\mathrm{L}])$ Here, F, F_0, k_f, k_s, K_a are fluorescence intensity, fluorescence of [10]CPP before the addition of C_{60}, a proportionality constant of the complex, a proportionality constant of the host, and the binding constant of C_{60}, respectively.
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