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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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

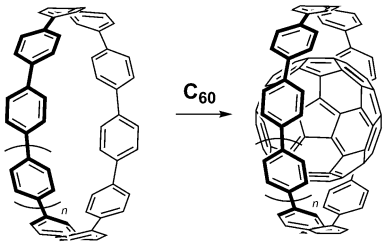

Figure 1. Structures of cycloparaphenylene (CPP) and C_{60} encapsulated CPP.

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

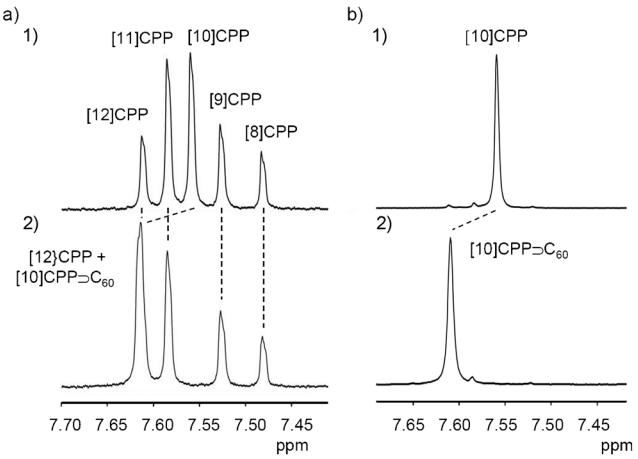

Figure 2. ^{1}H NMR spectra in $CDCl_3$ at room temperature of a) [8]–[12]CPPs before (1) and after (2) the addition of C_{60} and b) isolated [10]CPP before (1) and after (2) the addition of C_{60}.

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⊃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⊃C_{60} and very similar to those for [6](1,4)naphthyleneacetylene⊃C_{60},[4,17] which is the strongest host reported so far for C_{60} consisting of simple hydrocarbons.

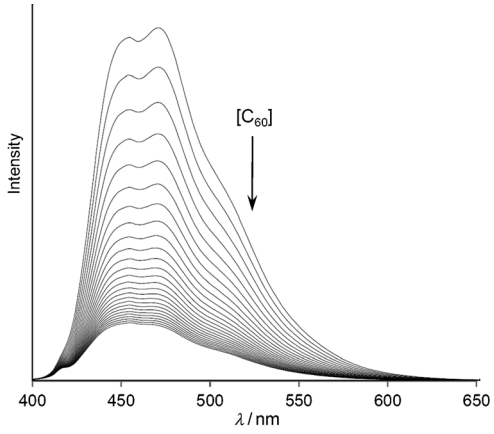

Figure 3. Fluorescence spectra of [10]CPP (5.13×10^{-7} mol L^{-1}, $\lambda_{exc} = 370$ nm) in the presence of C_{60} in toluene. The concentrations of C_{60} are 0.0–12.30 ($\times 10^{-7}$ mol L^{-1}) from the top to the bottom.

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⊃C_{60} at room temperature. Two singlets corresponding to free [10]CPP and [10]CPP⊃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⊃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⊃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⊃C_{60} even at low temperature, the paraphenylene unit in the complex must be structurally flexible and be rapidly fluttering at this temperature.

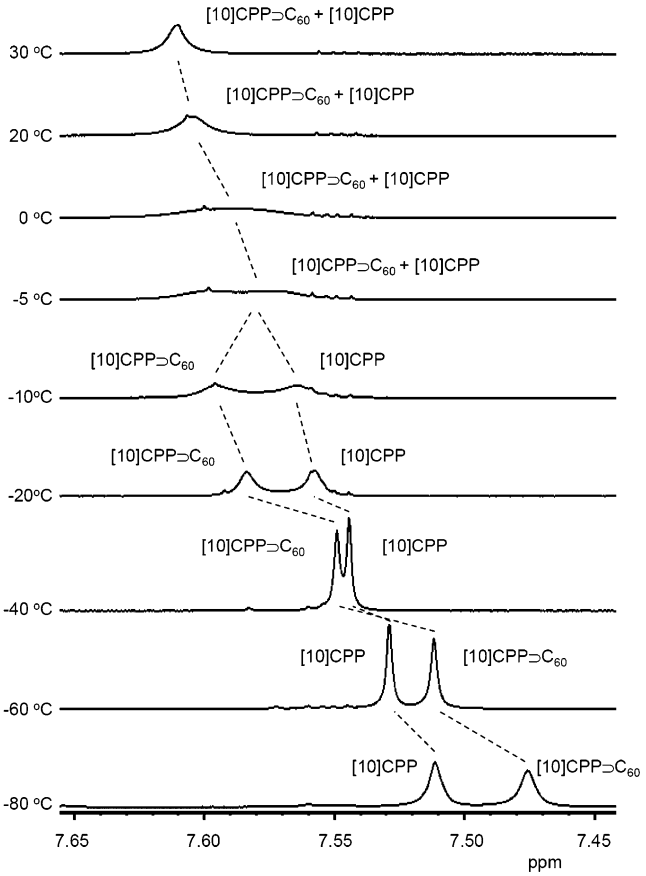

Figure 4. Variable-temperature ^{1}H NMR spectra of a 2:1 mixture of [10]CPP and C_{60} in CD_2Cl_2.

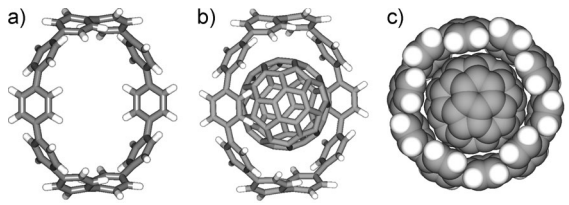

Figure 5. Structure of a) [10]CPP, b) [10]CPP⊃C_{60} complex (side view), and c) its space-filling model (top view) optimized at the M06-2X/6-31G* level of theory.

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⊃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 kJ mol^{-1}, respectively,[41] and these values are roughly 60 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] $F/F_0 = (1 + (k_f/k_s)K[L])/(1+K_a[L])$ 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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