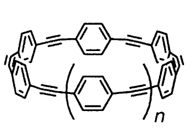
Supramolecular Dynamics

Complexation of Carbon Nanorings with Fullerenes: Supramolecular Dynamics and Structural Tuning for a Fullerene Sensor**

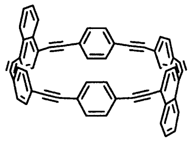
Takeshi Kawase, Kenji Tanaka, Yohko Seirai, Nami Shiono, and Masaji Oda**

Recently we have found that a carbon nanoring **1**, cyclic [6]paraphenyleneacetylene ([6]CPPA), which has a smooth belt-shaped structure with a 1.31 nm diameter, forms stable inclusion complexes with fullerenes (C_{60} and a methano[60]-fullerene derivative) in solution as well as in the solid state.[1] Although the host molecule is composed of only carbon and hydrogen atoms, the association constants are quite high ($> 10^4$).[2] From these results, together with crystallographic analysis, we concluded that the novel noncovalent interaction, namely concave–convex π–π interaction, plays an important role in the complexation.[3] The same interaction should also be important in the formation and properties of multiwalled carbon nanotubes,[4] Bucky onions[5] and "fullerene Peapods".[6] On the other hand, the molecular structure also reveals that the cavity size of **1** is slightly smaller than that of C_{60}. These findings promoted us to investigate the structural tuning of carbon nanorings for optimizing complexation with fullerenes (C_{60} and C_{70}).

We previously prepared "carbon nanorings" **1**–**4** ([6]–[9]CPPAs).[7] According to theoretical calculation (AM1 method),[8] the diameters of **2**, **3**, **4** are 1.53, 1.74, and 1.96 nm, respectively. We have designed new carbon nanorings **5** and **6**, isomers of **2**, which have 1,4- or 2,6-naphthylene units at diametrically opposed positions in place of 1,4-phenylene units of **1**. In contrast with **1**–**4**, rotational isomers are possible for **5** and **6**. While the cavity size of **5** is equal to that of **1**, the cavity sizes of **6** (1.41 nm for *syn*-**6** and 1.39 nm for *anti*-**6**) are between those of **1** (or **5**) and **2**. When the van der Waals distance between carbon atoms with sp^2 hybridized orbitals are taken into account (0.34 nm), the cavity of **6** is slightly larger than the C_{60} molecule but is just right to accommodate a C_{70} molecule. However, the cavity of **2** is slightly too large even for a C_{70} molecule (Figure 1c). Herein we report on the formation of unusually stable complexes of new carbon nanorings with fullerenes and their novel supramolecular dynamics based on NMR spectroscopic analysis. Moreover, we have found that these carbon nanorings can act as efficient fluorescence sensors for fullerenes, and that the host **6** is the best sensor known to date.



1; $n = 1$, **2**; $n = 2$
3; $n = 3$, **4**; $n = 4$



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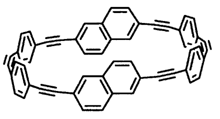

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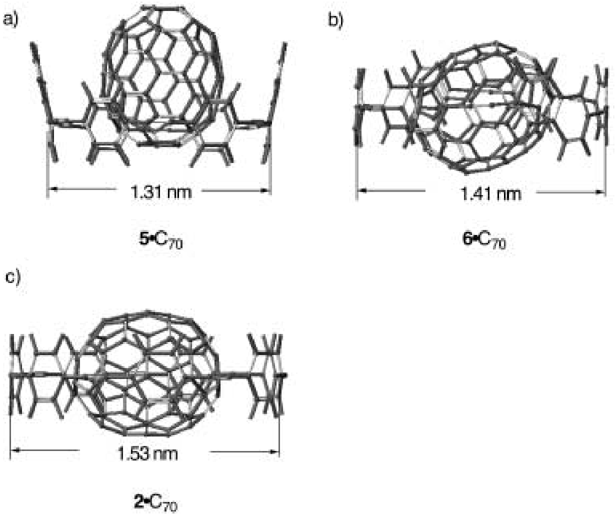

5•C_{70} **6**•C_{70} **2**•C_{70}

Figure 1. The optimized structures of **5**·C_{70}, **6**·C_{70}, and **2**·C_{70} by AM1 calculation.

Syntheses of **5** and **6** (see Table 1) were carried out as shown in Scheme 1. These compounds are susceptible to acid and oxygen, but stable enough to be stored in dilute solution

Table 1: Selected data for **5** and **6**

5:Yellow fine crystals, mp 120 °C (decomp); MS (FAB): $m/z = 700$ (M^+);IR-Raman (KBr): $\tilde{\nu} = 2189.86$ (C≡C, s), 2168.43 (C≡C, s), 1593.55 cm^{-1} (C=C, s); ^1H NMR (270 MHz, $CDCl_3$): $\delta = 7.36$ (AA′BB′, $J_{AB} = 8.6$ Hz, 8 H), 7.41 (AA′BB′, $J_{AB} = 8.6$ Hz, 8 H), 7.56 (s, 4 H), 7,58 (*m*-naphthyl, 4 H), 8.31 ppm (*m*-naphthyl, 4 H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 96.97$, 97.58, 100.55, 122.37, 123.83, 124.09, 126.47, 127.23, 129.35, 130.93, 130.97, 133.07 ppm; UV (cyclohexane): λmax [nm](log ε) = 354(5.14); Fluorescence (cyclohexane): λmax [nm] = 418, 448; quantum yields $\Phi = 0.24$;

6: Yellow fine crystals, mp > 97 °C (decomp); MS (FAB): $m/z = 700$ [M^+]; IR-Raman (KBr): $\tilde{\nu} = 2199.12$ (C≡C, m), 2184.19 (C≡C, s), 2160.56 (C≡C, w), 1592.27 cm^{-1} (C=C, s); ^1H NMR (270 MHz, $CDCl_3$): $\delta = 7.34$ (AA′BB′, $J_{AB} = 8{,}6$ Hz, 8 H), 7.38 (AA′BB′, $J_{AB} = 8.6$ Hz, 8 H), 7.44 (dd, $J = 1.3$, 8.6 Hz, 4 H), 7.67 (d, $J = 8.6$ Hz, 4 H), 7.83 ppm (d, $J = 1.3$ Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 96.88$, 97.10, 97.50, 121.75, 123.86, 124.02, 127.79, 128.82, 130.53, 130.91, 130.96, 132.89 ppm; UV (cyclohexane): λmax [nm](log ε) = 338(5.2) s, 358(5.4), 405(4.5); Fluorescence (cyclohexane): λmax [nm] = 472; quantum yields $\Phi = 0.20$.

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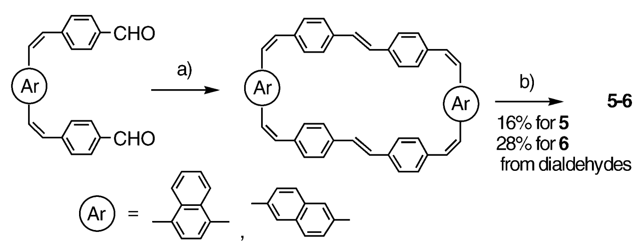

Scheme 1. Synthesis of **5** and **6**: a) $TiCl_4$-Zn(CuI), 1,2-dimethoxyethane/toluene (1:1), room temperature, 12 h, then reflux 6 h; b) Br_2, $CHCl_3$, RT, 6 h, then *t*BuOK, ether, room temperature, 12 h.

at 0 °C over a month. The NMR spectra of **5** and **6** at 30 °C reveal D_2 symmetry of the molecules, and the signals are almost unchanged even at −90 °C (in CD_2Cl_2) except for some slight broadening. The results clearly indicate that each aromatic ring rotates faster than the NMR time scale in the measurable temperature range.

The stability of fullerene complexes is generally evaluated in terms of the association constant (K_a) determined by absorption spectra.[9,10] The titration experiment of **1**·C_{70} determined the K_a value to be $(1.8\pm0.2)\times10^4\,dm^3mol^{-1}$, which is slightly larger than that of **1**·C_{60}, $(1.6\pm0.3)\times10^4\,dm^3mol^{-1}$. The rather small differences in the values of K_a, however, indicate that the symmetry mismatching between **1** (*D6h*) and C_{70} (*D5h*) is not an important factor for complexation. On the other hand, we have found that the K_a values for the complexes of **5** and **6** with fullerenes in benzene are too large ($>5\times10^4$) to be determined precisely.[10] The K_a value of **6**·C_{60} and **6**·C_{70}, in fact, can be roughly estimated to be about 1×10^5 and $1\times10^6\,dm^3mol^{-1}$, which would indicate that the host forms extremely stable complexes for a hydrocarbon.

In a previous paper,[1c] we described that variable-temperature NMR spectra of **1**·C_{60} in CD_2Cl_2 provide the Gibbs energies of activation ($\Delta G^{\neq}$) for the dissociation of the complex, and indicate the high mobility of the guest molecule in the cavity. Similarly, the ^{1}H NMR spectra of the complexes, **1**·C_{70}, **5**·C_{60}, **5**·C_{70}, and **6**·C_{70}, in CD_2Cl_2 at −100 °C revealed that the dissociation rates of these complexes also are slower than the NMR time scale. The variable-temperature NMR experiments thus afforded the $\Delta G^{\neq}$ values of these complexes (Table 2), and further important information about their supramolecular dynamics.[11]

Table 2: Coalescence temperatures (*Tc*) and $\Delta G^{\neq}$ values of the complexes.

complex	T_c[a]	$\Delta G^{\neq}$ (CD_2Cl_2)[b]
1·C_{60}	-80 ± 5	9.9 ± 0.2
1·C_{70}	-60 ± 5	9.6 ± 0.2
5·C_{60}	-50 ± 5	10.8 ± 0.3
5·C_{70}	-60 ± 5	10.1 ± 0.2
6·C_{60}	<-100	<9
6·C_{70}	-30 ± 10	11.9 ± 0.8
2·C_{60}	<-100	<9
2·C_{70}	<-100	<9

[a] °C. [b] $kcal\,mol^{-1}$.

Whereas the signal of **1**·C_{60} complex appears as a singlet at −100 °C, the ^{1}H NMR spectrum of complex **1**·C_{70} (1:1) has two singlets (7.484 and 6.929 ppm) of equal intensity at −90 °C (Figure 2). The $\Delta G^{\neq}$ value is estimated to be $(9.6\pm0.2)\,kcal\,mol^{-1}$ ($T_c=-60\pm5\,°C$) in CD_2Cl_2. The two signals show the presence of two sets of non-equivalent aromatic protons because the center of C_{70} is not aligned with the center of **1** (Figure 2). Thus, these results indicate that the activation energy of the passage of the C_{70} through the cavity of **1** is at least as high as the value of dissociation, which is in contrast to the case of complex **1**·C_{60}. In addition, the appearance of the signals as singlets again suggests fast rotation of C_{70} probably around the long axis. In the structure of **1**·C_{70}, which has lower symmetry than that of **1**·C_{60}, the inner and outer aromatic protons should receive a different anisotropic effect from C_{70}. The large barrier as well as the relatively large anisotropic effect would be attributable to the high π-electron density of the relatively flat midsection of C_{70}.[12]

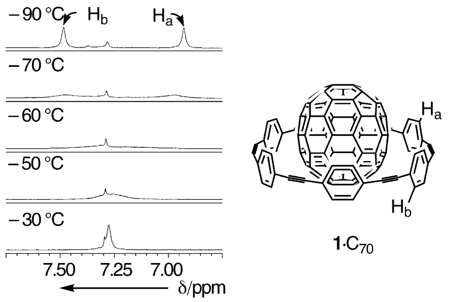

Figure 2. ^{1}H NMR spectra of a 1:1 mixture of **1** and C_{70}.

The spectra of **5**·C_{60} and **5**·C_{70} (Figure 3 a and b) show that these complexes exist in a mixture of *syn*- and *anti*-isomers at low temperatures, where the *syn*-isomers would be predominant probably because they have a wider contact area than the *anti*-isomers. The appearance of some aromatic signals of **5**·C_{70} at a relatively high magnetic field provides evidence for the assignment, because, according to the calculated molecular structure (Figure 1 b), the corresponding protons should receive the anisotropic effect of the midsection of C_{70}. In agreement with considerably high K_a value, the $\Delta G^{\neq}$ for dissociation of **6**·C_{70} ($11.9\pm0.8\,kcal\,mol^{-1}$) is the highest. However, the NMR spectra at low temperatures appear to be relatively simple (Figure 3 c), thus indicating the high mobility of the guest in the cavity. Unlike these complexes, the variable-temperature NMR spectra of **6**·C_{60}, **2**·C_{60} and **2**·C_{70} indicate that the $\Delta G^{\neq}$ values are immeasurably low ($<9\,kcal\,mol^{-1}$). The activation energies thus correlate with the van der Waals contact between the host and guest. In one of our previous papers,[1c] we pointed out the importance of the electrostatic attractive force between the concave and convex surfaces in addition to the dispersion force, because the high affinity between a carbon nanoring **1** and C_{60} can be hardly explained in terms of dispersion forces alone.[1c,3,13] The formation of the extremely stable complexes such as **6**·C_{70}

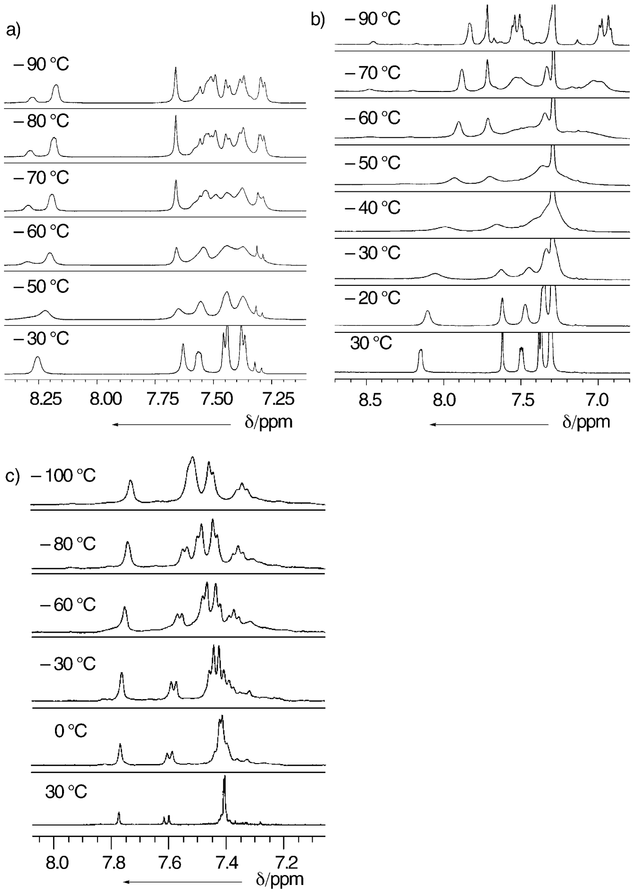

Figure 3. Temperature-variable NMR spectra of an equimolar solution of a) **5** and C_{60}, b) **5** and C_{70}, and c) **6** and C_{70}.

provides additional evidence for our conclusion, and also has the novel feature of a curved conjugated systems.

Furthermore, we have found that the presence of a fullerene quenches the intense fluorescence emission of CPPAs very effectively. We have monitored the titration experiments by means of fluorescence spectra to determine the Stern–Völmer constant (K_{SV}).[9] Although the K_{SV} values are not direct measures of the complexation because of the quenching mechanisms, they are informative in estimating the relative stability of these complexes.[14–16] Table 3 lists the K_{SV} values of the complexes. The order of the values are $\mathbf{5} \geq \mathbf{6} > \mathbf{1} > \mathbf{2} > \mathbf{3}$ for the C_{60} complexes, and $\mathbf{6} > \mathbf{5} > \mathbf{2} > \mathbf{1} > \mathbf{3}$ for the C_{70} complexes, respectively. The ratio of the K_{SV} values for $\mathbf{6}{\cdot}C_{70}/\mathbf{6}{\cdot}C_{60}$ is roughly consistent with the ratio of the K_a values for $\mathbf{6}{\cdot}C_{70}/\mathbf{6}{\cdot}C_{60}$ (K_a $\mathbf{6}{\cdot}C_{70}/\mathbf{6}{\cdot}C_{60} \approx 10$). It is noteworthy that **6** can act as the best fluorescence sensor for fullerenes among all the known hosts.[14]

Table 3: Diameters (Φ)[a] of the cavity of hosts and K_{SV} values[b] of the complexes.

	1	5	6	2	3
Φ	1.31	1.31	1.41	1.53	1.74
K_{SV} C_{60}	7.0×10^4	2.7×10^5	2.6×10^5	5.6×10^4	$<10^4$
K_{SV} C_{70}	1.4×10^5	2.6×10^5	4.3×10^6	2.1×10^5	$<10^4$
K_{C70}/K_{C60}	2.0	1.0	16.5	3.7	

[a] nm, evaluated by AM1 calculations. [b] $dm^3\,mol^{-1}$, in C_6H_6.

Moreover, the significantly larger K_a and K_{SV} values of $\mathbf{6}{\cdot}C_{70}$ than that of $\mathbf{6}{\cdot}C_{60}$ suggests that the complexation of **6** with C_{70} is highly selective; in fact, upon competitive complexation of **6** through solid-to-liquid extraction from a fullerite (C_{60}:C_{70} = about 1:1) in CD_2Cl_2, the NMR spectrum of the extract was almost identical to that of $\mathbf{6}{\cdot}C_{70}$, thus indicating the considerably high selectivity (> 10:1) for C_{70} against C_{60}.[17] A similar experiment with the host **1** shows a relatively low and inverse selectivity (1:4). These findings will also open the way to create tailor-made hosts for the separation of higher fullerenes and carbon nanotubes.

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[15] Quenching of the fluorescence takes place by an intermolecular energy-transfer process from the excited states of CPPAs to fullerenes. The Stern–Völmer plots show straight lines, which suggest the quenching mechanism through 1:1 complexes involve several mechanisms (Figure 4). Further investigation of the energy-transfer mechanisms of the systems will be reported in due course.

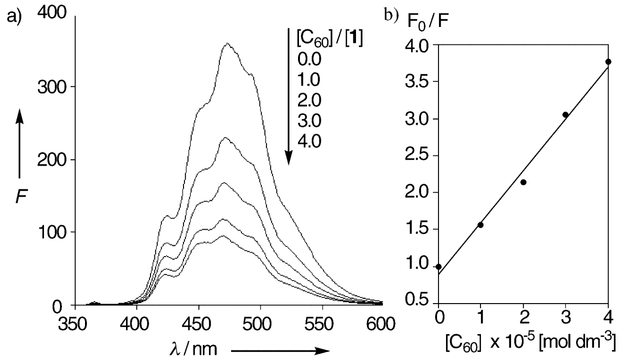

Figure 4. a) Emission spectral change of **1** in the presence of C_{60} in benzene. $\lambda_{excitation} = 363$ nm, $[\mathbf{1}] = 1.0 \times 10^{-5}$ mol dm^{-3} constant. $[C_{60}] = [\mathbf{1}] \times 0 \sim 4.0$ mol dm^{-3}. b) Stern–Völmer plot.

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