Noncovalent Interactions

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Cyclic [5]Paraphenyleneacetylene: Synthesis, Properties, and Formation of a Ring-in-Ring Complex Showing a Considerably Large Association Constant and Entropy Effect**

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The concave–convex π–π interaction between curved graphene sheets should be important for the formation and properties of new carbon materials such as bucky onions,[1] carbon nanotubes,[2] and fullerene peapods.[3] If the curved π-electron system is polarized owing to the unsymmetrical nature of its p orbital with respect to the convex and concave sides,[4] the two surfaces would exert some level of electrostatic attraction toward each other. Contrary to the intuitive prediction, the interlayer interaction of multiwalled carbon nanotubes has mainly been interpreted as a dispersion force.[5] Moreover, recent theoretical studies predicted the participation of a charge-transfer (CT) interaction between carbon nanotubes and neutral aromatic molecules.[6] However, the participation of electrostatic interactions has tended to be neglected.

Recently we reported the synthesis of cyclic [6]- to [9]paraphenyleneacetylenes ([6]- to [9]CPPA; **2**–**5**; Figure 1).[7] These compounds have smooth belt-shaped structures, in which the p orbitals are aligned perpendicular to a rigid surface, and thus may be termed "carbon nanorings". Compound **2**, with a diameter of 1.32 nm, forms an unusually stable inclusion complex with C_{60} [association constant $(K_a) = (1.6 \pm 0.3) \times 10^4\,\mathrm{L\,mol^{-1}}$ at 30°C in benzene].[8] We also found that **2** can be accommodated in the cavity of [9]CPPA (**5**), which has a diameter of 1.96 nm, to construct a ring-in-ring complex ($K_a \approx 40\,\mathrm{L\,mol^{-1}}$ at 30°C in $CDCl_3$).[9,10] Moreover, dibenzo[6]- and tribenzo[9]CPPAs (**6** and **7**) also form a ring-in-ring complex ($K_a = 470 \pm 80\,\mathrm{L\,mol^{-1}}$ at 30°C in $CDCl_3$). The greater K_a value results from the increased contact area of the component molecules. To explore the relationship between molecular strain and the properties of curved conjugated systems, we synthesized [5]CPPA (**1**), the smallest member of this class. When the van der Waals radii of the sp^2-hybridized carbon atoms are taken into account (0.34 nm), [8]CPPA (**4**; diameter $\varnothing = 1.74$ nm) is almost perfect complementarity to **1** ($\varnothing = 1.07$ nm). In comparison with **5**⊃**2** and **7**⊃**6**, **4**⊃**1** has a smaller contact area and both its component compounds are highly strained (Figure 1). The situation is analogous to that between **5**⊃**2** and **2**⊃C_{60}. Therefore, the complexation behavior should provide an insight into the nature of the concave–convex π–π interaction. We herein report the synthesis and properties of **1**, as well as its formation of a ring-in-ring complex with **4**.

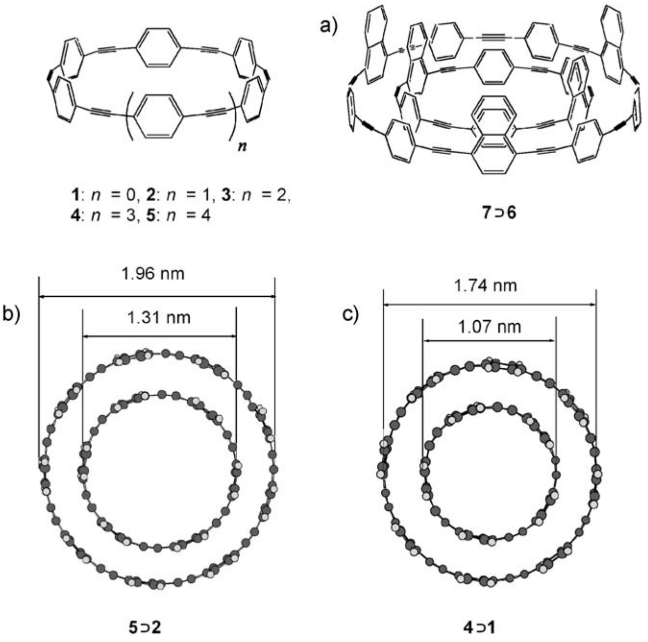

Figure 1. Structures of CPPAs **1**–**5** and ring-in-ring complexes: a) **7**⊃**6**, b) **5**⊃**2**, and c) **4**⊃**1**.

Bromination of [2.$_5$]paracyclophanepentaene with excess bromine and subsequent dehydrobromination of the crude perbromide with *t*BuOK in diethyl ether gave the desired compound **1** as yellow fine needles in 27% yield.[11] Hydrogenation of **1** with Pd/C in toluene afforded the known [2^5]paracyclophane[12] in moderate yield. [5]CPPA (**1**) is sensitive to oxygen both in solution and in the solid state. When exposed to the air, it decomposed rapidly to form amber-colored insoluble polymeric material. Its decomposition rate is faster than that of **2**. However, **1** could be purified by column chromatography on alumina and could be stored as a dilute solution under an inert atmosphere at 0°C for more than a week.

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Table 1: Selected spectral data of CPPAs **1**–**5**.

Compd	^{1}H NMR[a] δ [ppm]	^{13}C NMR[a] δ [ppm]			Absorption max. [nm][b,c]	Emission max. [nm][b,d]
1	7.15	101.17	125.34	130.28	346 (5.02)	449, 461
2	7.35	97.65	123.93	130.87	349 (5.40)	471
3	7.36	96.14	123.92	131.07	355 (5.41)	418, 448
4	7.40	94.95	123.67	131.21	355 (5.47)	416, 447
5	7.43	94.21	123.56	131.23	354 (5.51)	414, 442

[a] In $CDCl_3$. [b] In cyclohexane. [c] $\log\varepsilon$ [$M^{-1}cm^{-1}$] shown in brackets. [d] $\lambda_{excitation} = 363$ nm.

The ^{1}H and ^{13}C NMR spectra of **1** are simple, which is in agreement with the high symmetry of the molecule (Table 1). The sp-hybridized carbon atoms of **1** resonate at $\delta = 2.5$ ppm, which is at lower field relative to that of **2**. The chemical shifts of CPPAs are well correlated with their molecular strains. Figure 2 shows the electronic and fluorescent spectra of **1** together with those of **2**–**5**.[7c,13] The absorption and emission curves of CPPAs exhibit a gradual change with the number of phenylacetylene units. Those of **1** are considerably different from those of the corresponding acyclic phenyleneacetylene oligomers **8**,[7a,14] probably because of the increase in strain or the effect of cyclic conjugation. In contrast, the ^{1}H NMR spectra exhibit no alternate changes associated with a peripheral conjugation, because odd-numbered CPPAs are aromatic and even-numbered CPPAs are antiaromatic on the basis of their peripheral conjugation. The absorption and emission maxima of **1** are at 3–10 nm shorter wavelength than those of **2**, which is attributable to the decreased extent of conjugation. The results indicate that the cyclic systems appear to be saturated from the heptamer stages, whereas the acyclic oligomers are saturated from the pentamer stage (see the Supporting Information).

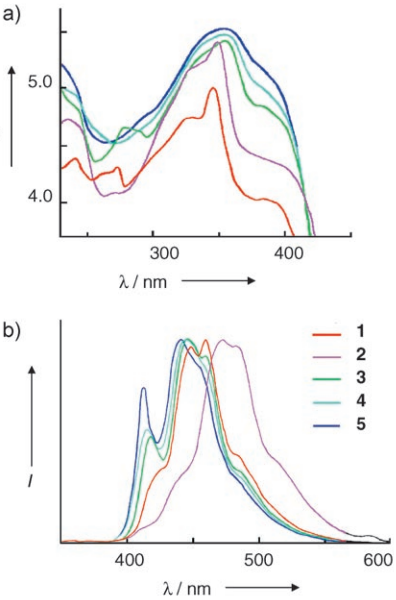
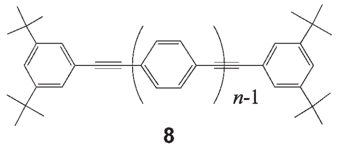


Figure 2. a) Absorption and b) normalized emission spectra of CPPAs **1**–**5** in cyclohexane.



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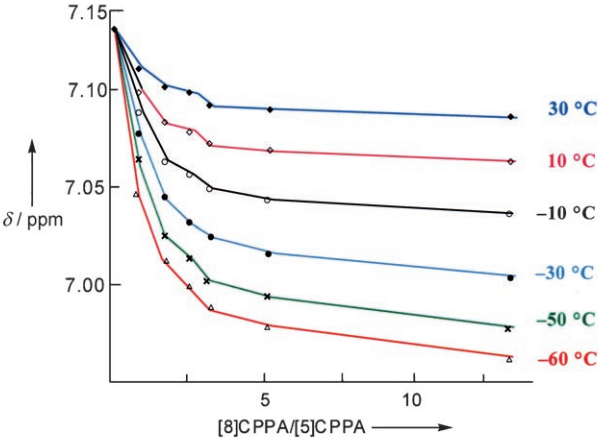

Figure 3. Plots of chemical shift (δ) of [5]CPPA (**1**) (1.38×10^{-4} M) in $CDCl_3$ versus added [8]CPPA (**4**) at various temperatures.

To explore the supramolecular properties of **1**, we examined its complexation with [8]CPPA (**4**) in chloroform. The ^{1}H NMR chemical shift of **1** appears at higher field as a mixture with **4** than in the pure form. It also varies with temperature and compound ratio (Figure 3); in contrast, the chemical shift of **4** shifts to slightly lower field. These results clearly indicate the formation of inclusion complex **4**$\supset$**1** in solution. K_a values of **1** at various temperatures were determined from the variation of the chemical shift in titration experiments (Table 2).[15] The thermodynamic parameters were calculated from the K_a values at various temperatures to be $\Delta H = 0.75$ kcal mol^{-1} and $\Delta S = 16$ cal mol^{-1}K^{-1}. The K_a value at 30 °C is about 200 times larger than that of **5**$\supset$**2**. The results indicate the substantial participation of the electrostatic interaction prior to the dispersion force. The ΔS value of **4**$\supset$**1** is significantly large in comparison with the value of **7**$\supset$**6** ($\Delta H = -4.5$ kcal mol^{-1} and $\Delta S = -2.4$ cal mol^{-1}K^{-1}).[9] The results indicate that **1** is tightly solvated by solvent molecules, probably because of the high molecular strain. The surface properties of **1** seem similar to those of fullerene.[16]

Recent theoretical and experimental studies on fullerene complexes predicted that the strong host–guest interactions are largely the result of dispersion force and are enhanced by weak electrostatic interactions.[17,18] A number of studies proposed that the electrostatic difference between 5:6 and 6:6 ring fusions play an important role in the electrostatic interaction.[19] Herein we have shown, however, that the K_a value of **4**$\supset$**1** is almost comparable to that of **2**$\supset C_{60}$. This

Table 2: Association constants (K_a) and ΔG values of **4**$\supset$**1** at various temperatures in $CDCl_3$.

T [°C]	$K_a\times10^{-3}$ [L mol^{-1}]	ΔG [kcal mol^{-1}]
30	9.2 ± 1.4	−5.51
10	11 ± 1.8	−5.23
−10	11 ± 1.7	−4.89
−30	12 ± 2.2	−4.55
−50	13 ± 0.7	−4.20
−60	15 ± 2.1	−4.08

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result indicates that the high affinity between concave–convex π surfaces is not limited to fullerene complexes. Planar phenylacetylene macrocycles without electron-withdrawing substituents on their aromatic rings do not aggregate in nonpolar solvents,[20] because π–π stacking between planar aromatic hydrocarbons causes an electrostatically repulsive force.[21] On the basis of these results, the concave–convex π–π interaction should vary from repulsive to attractive with an increase in strain of the π-electron system. The drastic increase of the association constants from **5**⊃**2** to **2**⊃C_{60} or **4**⊃**1** can be explained in terms of the participation of the additional electrostatic interaction corresponding to the increasing polarity of the π systems.

The attractive interactions would also play an important role in the spontaneous formation of fullerene peapods and other new materials based on carbon nanotubes. Further experimental and theoretical studies on these compounds and related substances will deepen our understanding of the nature of fullerene and the other curved π-electron systems.[22]

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