Electronic Supplementary Information

Molecular Bearing of Finite Carbon Nanotube and Fullerene in Ensemble Rolling Motion

Hiroyuki Isobe*, Shunpei Hitosugi, Takashi Yamasaki, and Ryosuke Iizuka

Department of Chemistry, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

*e-mail: isobe@m.tohoku.ac.jp

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Supplementary Figures



Figure S1. ¹H NMR spectra, structures and symmetry of vacant [4]CC isomers.¹ (a) Spectra of [4]CC isomers in CDCl₃ at 25 °C. The assignments of the positions for the aromatic protons were enabled by the apparent differences in the coupling patterns: Doublet of doublet for H³ and H⁹ (blue), doublet for H¹ and H⁷ (pink), singlet for H⁵ and H¹¹ (orange), and doublet for H⁴ and H¹⁰ (green). Among these resonances, the doublets of H⁴ and H¹⁰ at the separated downfield region provided characteristic signatures of the symmetry. Each [4]CC isomer bears eight protons of these positions, and the numbers of the signature resonances from H⁴/H¹⁰ are shown. (b) Structures and symmetry operations of [4]CC isomers. The signature protons of H⁴/H¹⁰ are shown in sphere with the identical green colors for the equivalent protons. The numbers of symmetrically equivalent protons are shown, which perfectly matches with the observed numbers.

¹ S. Hitosugi, W. Nakanishi, T. Yamasaki, H. Isobe, Nat. Commun., 2011, 2, doi: 10.1038/ncomms1505.



Figure S2. Aromatic resonances of ¹H NMR spectra of (*P*)-(12,8)-[4]CC \supset C₆₀, showing two independent sets of aromatic resonances in 2:1 mixture. (a) A reference spectrum from 1:1 mixture of (*P*)-(12,8)-[4]CC and C₆₀. (b) A spectrum from 2:1 mixture of (*P*)-(12,8)-[4]CC and C₆₀. (c) A reference spectrum of vacant (*P*)-(12,8)-[4]CC. All the spectra were recorded in CDCl₃ at 25 °C.



Figure S3. Aromatic resonances of ¹H NMR spectra of (*P*)-(12,8)-[4]CC \supset C₆₀ at -60 °C. (a) A reference spectrum of vacant (*P*)-(12,8)-[4]CC in CD₂Cl₂ at -60 °C. (b) A spectrum of (*P*)-(12,8)-[4]CC \supset C₆₀ in CD₂Cl₂ at -60 °C.

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Figure S4. Fluorescence quenching titration experiments for (*P*)-(12,8)-[4]CC \supset C₆₀ in *o*DCB. (a) A representative fluorescence spectral change of (*P*)-(12,8)-[4]CC at 2.00 × 10⁻⁹ M during the titration of C₆₀ at 2.00 × 10⁻⁸ M. Excitation = 368 nm. (b) Spectral change at the fluorescence maximum. A curve from the fitting analysis is shown along with the log *K*_a value and the *R*² measure for the goodness-of-fit.



Figure S5. Fluorescence quenching titration experiments for (*P*)-(11,9)-[4]CC \supset C₆₀ in *o*DCB. (a) A representative fluorescence spectral change of (*P*)-(11,9)-[4]CC at 2.00 × 10⁻⁹ M during the titration of C₆₀ at 2.00 × 10⁻⁸ M. Excitation = 369 nm. (b) Spectral change at the fluorescence maximum. A curve from the fitting analysis is shown along with the log K_a value and the R^2 measure for the goodness-of-fit.

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Figure S6. Fluorescence quenching titration experiments for $(10,10)_{AABB}$ -[4]CC \supset C₆₀ in *o*DCB. (a) A representative fluorescence spectral change of $(10,10)_{AABB}$ -[4]CC at 2.00 × 10⁻⁹ M during the titration of C₆₀ at 2.00 × 10⁻⁸ M. Excitation = 367 nm. (b) Spectral change at the fluorescence maximum. A curve from the fitting analysis is shown along with the log K_a value and the R^2 measure for the goodness-of-fit.



Figure S7. Fluorescence quenching titration experiments for $(10,10)_{ABAB}$ -[4]CC \supset C₆₀ in *o*DCB. (a) A representative fluorescence spectral change of $(10,10)_{ABAB}$ -[4]CC at 2.00 × 10⁻⁹ M during the titration of C₆₀ at 2.00 × 10⁻⁸ M. Excitation = 371 nm. (b) Spectral change at the fluorescence maximum. A curve from the fitting analysis is shown along with the log K_a value and the R^2 measure for the goodness-of-fit.

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Figure S8. Fluorescence quenching titration experiments for (+)-(16,0)-[4]CC \supset C₆₀ in *o*DCB. (a) A representative fluorescence spectral change of (+)-(16,0)-[4]CC at 8.50 × 10⁻⁶ M during the titration of C₆₀ at 8.30 × 10⁻⁴ M. Excitation = 359 nm. (b) Spectral change at the fluorescence maximum. A curve from the fitting analysis is shown along with the log K_a value and the R^2 measure for the goodness-of-fit.



Figure S9. Fluorescence quenching titration experiments for (*P*)-(12,8)-[4]CC \supset C₆₀ in C₁₁H₁₀ (1-methylnaphthalene). (a) A representative fluorescence spectral change of (*P*)-(12,8)-[4]CC at 8.01 × 10⁻⁹ M during the titration of C₆₀ at 8.00 × 10⁻⁸ M. Excitation = 369 nm. (b) Spectral change at the fluorescence maximum. A curve from the fitting analysis is shown along with the log *K*_a value and the *R*² measure for the goodness-of-fit.

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Figure S10. Fluorescence quenching titration experiments for (*P*)-(12,8)-[4]CC \supset C₆₀ in PhCl. (a) A representative fluorescence spectral change of (*P*)-(12,8)-[4]CC at 1.86 × 10⁻⁹ M during the titration of C₆₀ at 2.04 × 10⁻⁸ M. Excitation = 368 nm. (b) Spectral change at the fluorescence maximum. A curve from the fitting analysis is shown along with the log *K*_a value and the *R*² measure for the goodness-of-fit.



Figure S11. Fluorescence quenching titration experiments for (*P*)-(12,8)-[4]CC \supset C₆₀ in CH₂Cl₂. (a) A representative fluorescence spectral change of (*P*)-(12,8)-[4]CC at 9.65 × 10⁻¹⁰ M during the titration of C₆₀ at 9.58 × 10⁻⁹ M. Excitation = 365 nm. (b) Spectral change at the fluorescence maximum. A curve from the fitting analysis is shown along with the log K_a value and the R^2 measure for the goodness-of-fit.

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Figure S12. Fluorescence quenching titration experiments for (*P*)-(12,8)-[4]CC \supset C₆₀ in CHCl₃. (a) A representative fluorescence spectral change of (*P*)-(12,8)-[4]CC at 4.59 × 10⁻¹⁰ M during the titration of C₆₀ at 4.38 × 10⁻⁹ M. Excitation = 366 nm. (b) Spectral change at the fluorescence maximum. A curve from the fitting analysis is shown along with the log K_a value and the R^2 measure for the goodness-of-fit.



Figure S13. Fluorescence quenching titration experiments for (*P*)-(12,8)-[4]CC \supset C₆₀ in toluene. (a) A representative fluorescence spectral change of (*P*)-(12,8)-[4]CC at 7.32 × 10⁻¹¹ M during the titration of C₆₀ at 7.32 × 10⁻¹⁰ M. Excitation = 365 nm. (b) Spectral change at the fluorescence maximum. A curve from the fitting analysis is shown along with the log K_a value and the R^2 measure for the goodness-of-fit.

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Figure S14. Fluorescence quenching titration experiments for (*P*)-(12,8)-[4]CC \supset C₆₀ in benzene. (a) A representative fluorescence spectral change of (*P*)-(12,8)-[4]CC at 8.12 × 10⁻¹⁰ M during the titration of C₆₀ at 8.01 × 10⁻⁹ M. Excitation = 366 nm. (b) Spectral change at the fluorescence maximum. A curve from the fitting analysis is shown along with the log K_a value and the R^2 measure for the goodness-of-fit.



Figure S15. Job plot analysis for (*P*)-(12,8)-[4]CC \supset C₆₀ in *o*DCB. (a) UV-vis spectra. (b) Job plot at total concentration of 5.14 × 10⁻⁶ M.



Figure S16. Job plot analysis for (+)-(16,0)-[4]CC \supset C₆₀ in *o*DCB. (a) UV-vis spectra. (b) Job plot at total concentration of 8.46 × 10⁻⁵ M.



Figure S17. A representative ITC diagram for (*P*)-(12,8)-[4]CC \supset C₆₀ in *o*DCB. (a) Titration raw data. (b) Curve analysis from ORIGIN program of the instrument. The error of ΔH from the triplicate experiments was ±0.3 and that from the measurements was ±0.1.



Figure S18. A representative ITC diagram for (*P*)-(12,8)-[4]CC \supset C₆₀ in C₁₁H₁₀ (1-methylnaphthalene). (a) Titration raw data. (b) Curve analysis from ORIGIN program of the instrument. The error of ΔH from the triplicate experiments was ±0.3 and that from the measurements was ±0.1.



Figure S19. A representative ITC diagram for (*P*)-(12,8)-[4]CC \supset C₆₀ in PhCl. (a) Titration raw data. (b) Curve analysis from ORIGIN program of the instrument. The error of ΔH from the triplicate experiments was ±0.2 and that from the measurements was ±0.2.



Figure S20. A representative ITC diagram for (*P*)-(12,8)-[4]CC \supset C₆₀ in CH₂Cl₂. (a) Titration raw data. (b) Curve analysis from ORIGIN program of the instrument. The error of ΔH from the triplicate experiments was ±0.4 and that from the measurements was ±0.1.



Figure S21. A representative ITC diagram for (*P*)-(12,8)-[4]CC \supset C₆₀ in CHCl₃. (a) Titration raw data. (b) Curve analysis from ORIGIN program of the instrument. The error of ΔH from the triplicate experiments was ±0.2 and that from the measurements was ±0.4.



Figure S22. A representative ITC diagram for (*P*)-(12,8)-[4]CC \supset C₆₀ in toluene. (a) Titration raw data. (b) Curve analysis from ORIGIN program of the instrument. The error of ΔH from the triplicate experiments was ±0.1 and that from the measurements was ±0.0.



Figure S23. A representative ITC diagram for (*P*)-(12,8)-[4]CC \supset C₆₀ in benzene. (a) Titration raw data. (b) Curve analysis from ORIGIN program of the instrument. The error of ΔH from the triplicate experiments was ±0.4 and that from the measurements was ±0.1.



Figure S24. ¹H NMR spectra of (*P*)-(12,8)-[4]CC \supset C₆₀ in CD₂Cl₂ at 25 °C.



Figure S25. ¹H NMR spectra of (*P*)-(12,8)-[4]CC⊃1 in CD₂Cl₂ at 25 °C.

Supplementary Methods

Synthesis. The compounds were synthesized by the methods reported in the literature.^{1,2,3}

Fluorescence quenching titration experiments. After the examination of several possible analytical methods.⁴ we found the fluorescence quenching titration experiment to be the most sensitive and reliable method for the present system and indeed was the method through which the association constants and the accompanying Gibbs free energy changes were determined.⁵ Although the effect was negligible except for (+)-(16,0)-[4]CC with a small log K_a , the fluorescent intensities were calibrated with the competitive C_{60} absorbance.⁶ The data for the calibration are shown in Table S1. A typical procedure for (P)-(12,8)-[4]CC is described: An aliquot of C₆₀ (50 μ L, 2.00 × 10⁻⁸ M) in *o*DCB was added to a solution of (*P*)-(12,8)-[4]CC (2.5 mL, 2.00 × 10⁻⁹ M) in a cuvette with the same medium at 25 °C on a spectrometer (F-7000, Hitachi High-Tech). After stirring the mixture for 1 min, the fluorescence was recorded with excitation at the absorption maximum (368 nm). The addition of C_{60} solution was repeated for 15 times, and the spectral changes in the fluorescence maximum (481 nm) were collected (Figure S4). The change in the fluorescence intensity was analyzed by the reported equation.⁵ The titration experiments were conducted in triplicate to obtain the mean value with the error in standard deviation (s.d.). The same procedure was applied to the other [4]CC compounds $[(P)-(11,9)-, (10,10)_{ABB}-, (10,10)_{ABAB}-, (10$ and (+)-(16,0)-[4]CC] (Figure S5-S8) and (P)-(12,8)-[4]CC in various solvent (Figure S9-S14). The results are summarized in Figure 1 and Table 1.

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[4]CC	solvent	$\lambda_{excitation}$	ε ([4]CC)	ε (C ₆₀)	$\lambda_{emission}$	ε (C ₆₀)
			at $\lambda_{excitation}$	at $\lambda_{excitation}$		at $\lambda_{emission}$
(12,8)	oDCB	368 nm	163000	15600	481 nm	1080
(11,9)	oDCB	369 nm	161000	15000	488 nm	1200
(10,10) _{AABB}	oDCB	367 nm	137000	16100	488 nm	1200
(10,10) _{ABAB}	oDCB	371 nm	133000	13900	490 nm	1240
(16,0)	oDCB	359 nm	86000	21600	434 nm	776
(12,8)	$C_{11}H_{10}$	369 nm	151000	17900	490 nm	1600
(12,8)	PhCl	368 nm	167000	11100	480 nm	430
(12,8)	CH_2Cl_2	365 nm	175000	9870	481 nm	564
(12,8)	CHCl ₃	366 nm	163000	15200	480 nm	1390
(12,8)	toluene	365 nm	187000	15900	478 nm	483
(12,8)	benzene	366 nm	172000	12600	480 nm	365

Table S1. Photophysical data for the fluorescence calibration

Job plot analysis of the association stoichiometry. The stoichiometry of the peapod formation was determined using (*P*)-(12,8)- and (+)-(16,0)-[4]CC as the representative specimen with Job plot analysis with UV-vis absorption spectra.⁴ Under the constraint of a fixed total concentration of 5.14×10^{-6} M, a mixture of (*P*)-(12,8)-[4]CC and C₆₀ was prepared in *o*DCB at various molar ratios (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 0:10), and the UV-vis absorption spectra of the mixtures were recorded at 25 °C (V-670, JASCO) (Figure S15). The absorbance at 368 nm was plotted to reveal a 1:1 stoichiometry. The same procedure was used for (+)-(16,0)-[4]CC at a fixed total concentration of 8.50×10^{-5} M, and the Job plot at the absorption maximum (400 nm) also confirmed the 1:1 stoichiometry (Figure S16). Note that the difference in the two Job plots (Figure S15b *vs.* S16b) is due to the stark difference in the association constants of two specimens and does not affect the results.

calorimetry (ITC) analysis. The Isothermal titration enthalpy gain (ΔH) for (P)-(12,8)-[4]CC \supset C₆₀ formation was measured by the ITC analysis using a microcalorimeter (MicroCal VP-iTC, GE Healthcare). All of the solvents were degassed prior to the analysis. Typically, a solution of (P)-(12,8)-[4]CC (1.48 \times 10⁻⁵ M in oDCB) was introduced into the microcalorimeter, and a solution of C_{60} (1.48 × 10⁻⁴ M in *o*DCB) was placed in a syringe for the automated titration. The addition of C₆₀ solution was continued until the ITC curve indicated saturation, and the enthalpy difference upon peapod formation was derived using the ORIGIN software program installed in the instrument. The entropy difference (ΔS) was estimated with the ΔH value in addition to the ΔG values from the fluorescence experiments. The titration experiments were conducted in triplicate for each solvent, and the errors were obtained in s.d. Representative ITC diagrams are shown in Figures S17-S23, and the results are summarized in Table 1. Attempts to derive the thermodynamics parameters directly by ITC analysis were not successful, because an ideal sigmoidal curve was not obtained due to the large association constants that exceeded measurement limits (log $K_a \sim 9$). Competition experiments with functionalized fullerenes⁷ were neither successful due to the minute difference in the enthalpy differences.

NMR analysis. All of the solutions were degassed by a freeze-thaw method prior to the analysis. A (*P*)-(12,8)-[4]CC \supset C₆₀ peapod solution was prepared by mixing (*P*)-(12,8)-[4]CC (0.90 mg, 0.57 µmol) and C₆₀ (0.41 mg, 0.57 µmol) in CD₂Cl₂ (*ca.* 0.5 mL) and analyzed on a spectrometer (Bruker AVANCE400) at temperatures ranging from 25 °C to -60 °C (Figure 2, S3 and S24). A solution of (*P*)-(12,8)-[4]CC \supset 1 was prepared by mixing (*P*)-(12,8)-[4]CC (3.6 mg, 2.3 µmol) and 1 (1.8 mg, 2.3 µmol) and subsequently adding deuterated trifluoroacetic acid (*ca.* 5 µL, 67 µmol) and analyzed as previously described (Figure 2 and S25).

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