Complexation study of a 1,3-phenylene-bridged cyclic hexa-naphthalene with fullerenes C_{60} and C_{70} in solution and 1D-alignment of fullerenes in the crystals

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Table of Contents

Instrumentation and Materials

^{1}H NMR (600 MHz) spectra were taken on a JEOL ECA-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to toluene as an internal reference for ^{1}H NMR (δ = 2.10 ppm).

X-ray crystallographic data were recorded at 103 K with a BRUKER-APEX II X-ray diffractometer using graphite monochromated Mo-Kα radiation equipped with a large area CCD detector. The structure was solved by using direct methods (SHELXT program).[S1] Structure refinements were carried out by using SHELXL-2014/7 program.[S2]

Figs. 2a, 3a, 5, S1, S4 and S7 were generated using KaleidaGraph (version 5.0.6). The curve-fitting (Figs. 2b, 3b, S2, S3, S5 and S6) was performed using the Bindfit program.[S3] Figs. 4a and 4b were generated using ORTEP-3 for Windows program.[S4] Figs. 4c, S9 and S10 were generated using Mercury 2023.2.0.[S5]

Flash-Photolysis Time-Resolved Microwave Conductivity (FP-TRMC)

Transient conductivity was measured by FP-TRMC systems. A resonant cavity was used to obtain a high degree of sensitivity in the measurement of conductivity. The resonant frequency and the microwave power were set at ~9.1 GHz and 3 mW, respectively, so that the electric field of the microwave was sufficiently small not to disturb the motion of charge carriers. The value of conductivity is converted to the product of the quantum yield (ϕ) and the sum of charge carrier mobilities ($\Sigma\mu$), by the following equation;

$$\phi\Sigma\mu = \frac{1}{e \cdot A \cdot I_0 \cdot F_{Light}} \cdot \frac{\Delta P_r}{P_r} \quad \text{(S1)}$$

where e, A, I_0, F_{Light}, ΔP_r, and P_r are the unit charge of a single electron, a sensitivity factor [(S/m)$^{-1}$], the incident photon density of the excitation laser (photons m^{-2}), a correction (or filling) factor (/m), the change in reflected microwave power, and the power of the reflected microwave radiation, respectively. The change of conductivity is equivalent with $\Delta P_r/(AP_r)$. Third-harmonic generation (THG, 355 nm) of a Nd:YAG laser (5-8 ns pulse duration) was used as an excitation source. The photon densities were set to 9.1×10^{15} photons cm^{-2} for the conductivity measurement of single crystals (Fig. 5). The experiments were carried out at room temperature in air.

Procedure of the ^{1}H NMR titration

Ten samples were prepared by mixing toluene-d_8 solutions of **N6** (4.0×10^{-4} M) and C_{60} (4.0×10^{-4} M) in different ratios (from 10:0 to 1:9) to make a total volume of 0.80 ml. The resulting solutions were subjected to ^{1}H NMR spectroscopy at 298 K (Fig. S1). ^{1}H-NMR spectrum was recorded for each sample, and the peaks at 7.64, 7.53 and 7.40 ppm were monitored.

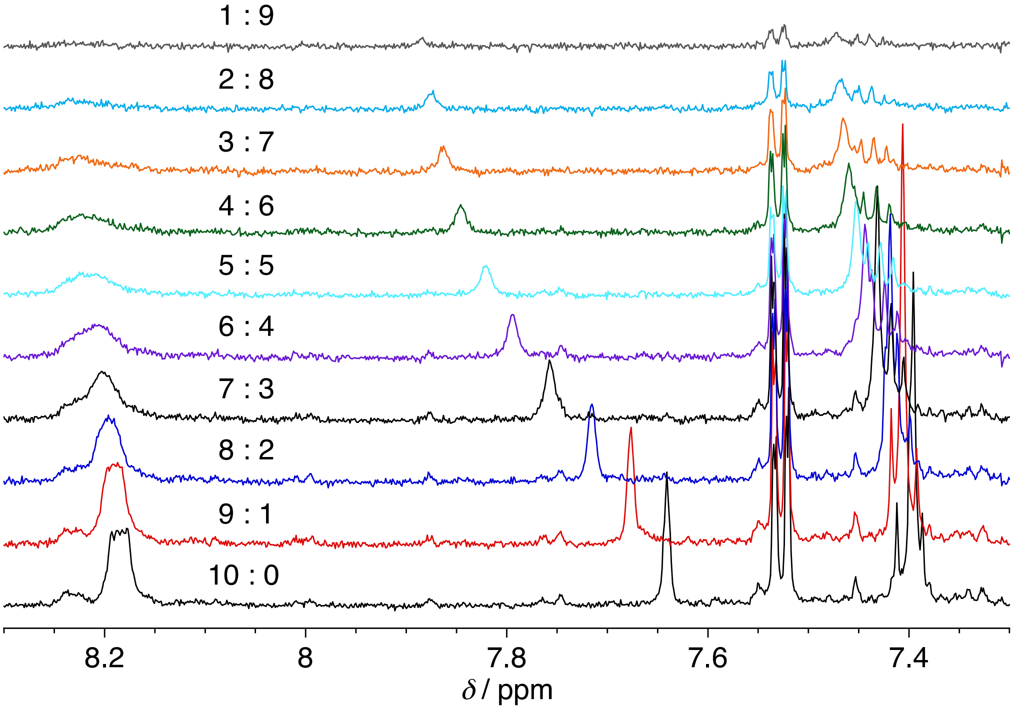

Fig. S1. ^{1}H NMR titration spectra of **N6** with C_{60} in toluene-d_8 at 298 K. [**N6**] : [C_{60}] = 10:0 to 1:9.

Fitting data for three different models (1:1, 1:2 and 2:1 binding models) were evaluated by AIC using a following equation,[S6]

$$\mathrm{AIC} = N \ln\left(\frac{SSR}{N}\right) + 2k$$

where N is the number of data points, SSR is the sum of squared residuals, and k is the number of parameters. The AIC values were calculated on the basis of the Bindfit program[S3] results.

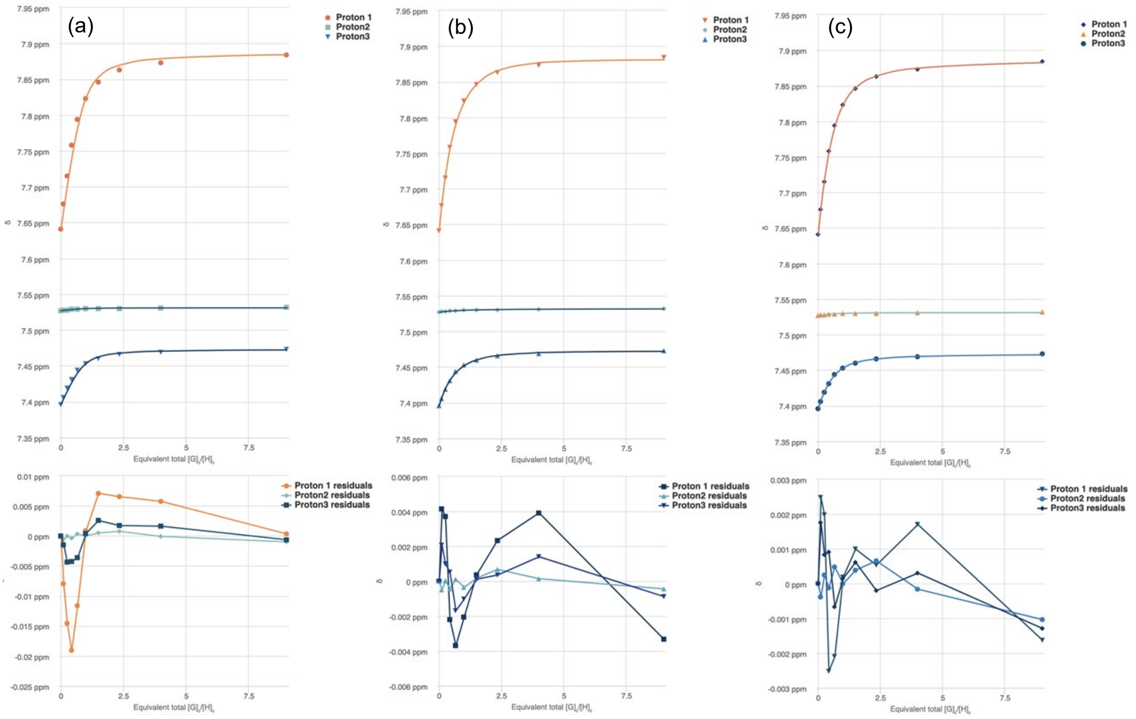

Fig. S2. Plots of chemical shift change of three different peaks (the initial data points: 7.64, 7.53 and 7.40 ppm, 10 samples, total data points $N = 30$) *versus* [C_{60}]/[**N6**]. Nonlinear curve regression of the titration of **N6** with C_{60} using (a) 1:1 binding model, (b) 1:2 non-cooperative model and (c) 2:1 additive model, associated with the Bindfit program. The curve-fit equations were defined in the literature.[S7]

Table S1. Different binding models for **N6** and C_{60} (the number of data points: $N=30$)[S3]

Binding model	Relationship between		K_1 or K_{11} (M^{-1})	K_{12} or K_{21} (M^{-1})	k	SSR	AIC
	K_1 and K_2	$\delta_{\Delta\mathrm{HG2}(\mathrm{or}\,\Delta\mathrm{H2G})}$ and $2\delta_{\Delta\mathrm{HG}}$					
1 : 1	K_1	$\delta_{\Delta\mathrm{HG}}$	3.68×10^{4} (±18%)	-	4	9.68×10^{-4}	–302
1:2 (full)	$K_1 \neq 4K_2$	$\delta_{\Delta\mathrm{HG2}} \neq 2\delta_{\Delta\mathrm{HG}}$	-	-	8	-	-
1:2 (noncooperative)	$K_1 = 4K_2$	$\delta_{\Delta\mathrm{HG2}} \neq 2\delta_{\Delta\mathrm{HG}}$	3.06×10^{3} (±2.8%)	7.65×10^{2} (±2.8%)	7	9.92×10^{-5}	–365
1:2 (additive)	$K_1 \neq 4K_2$	$\delta_{\Delta\mathrm{HG2}} = 2\delta_{\Delta\mathrm{HG}}$	-	-	5	-	-
1:2 (statistical)	$K_1 = 4K_2$	$\delta_{\Delta\mathrm{HG2}} = 2\delta_{\Delta\mathrm{HG}}$	-	-	4	-	-
2:1 (full)	$K_1 \neq 4K_2$	$\delta_{\Delta\mathrm{H2G}} \neq 2\delta_{\Delta\mathrm{HG}}$	-	-	8	-	-
2:1 (noncooperative)	$K_1 = 4K_2$	$\delta_{\Delta\mathrm{H2G}} \neq 2\delta_{\Delta\mathrm{HG}}$	-	-	7	-	-
2:1 (additive)	$K_1 \neq 4K_2$	$\delta_{\Delta\mathrm{H2G}} = 2\delta_{\Delta\mathrm{HG}}$	1.69×10^{4} (±3.7%)	4.54×10^{2} (±9.3%)	5	3.70×10^{-5}	–398
2:1 (statistical)	$K_1 = 4K_2$	$\delta_{\Delta\mathrm{H2G}} = 2\delta_{\Delta\mathrm{HG}}$	2.48×10^{3} (±2.1%)	6.20×10^{2} (±2.1%)	4	3.22×10^{-4}	–335

The $\delta_{\Delta\mathrm{HG}}$, $\delta_{\Delta\mathrm{HG2}}$ and $\delta_{\Delta\mathrm{H2G}}$ denote the changes in the NMR resonances of interest upon forming a 1:1 ($\delta_{\Delta\mathrm{HG}}$), 1:2 ($\delta_{\Delta\mathrm{HG2}}$) and 2:1 ($\delta_{\Delta\mathrm{H2G}}$) complex, respectively. K_{11}: the first stepwise association constant. K_{12} and K_{21}: the second stepwise association constants for 1:2 and 2:1 binding systems, respectively.

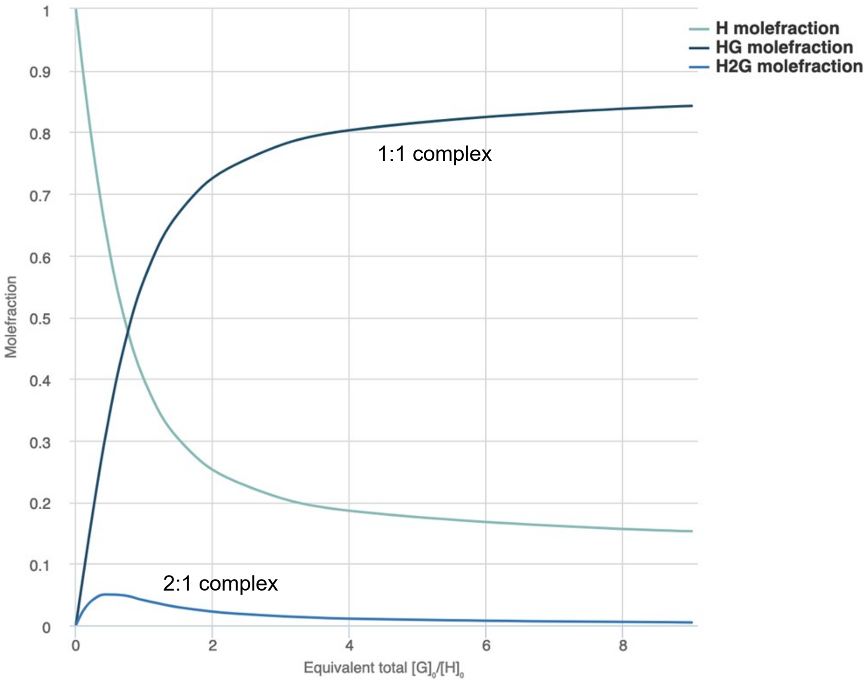

Fig. S3. Species evolution upon titration of C_{60} using the stoichiometric 2:1 additive binding model.[S7]

Ten samples were prepared by mixing toluene-d_8 solutions of **N6** (4.0×10^{-4} M) and C_{70} (4.0×10^{-4} M) in different ratios (from 10:0 to 1:9) to make a total volume of 0.80 ml. The resulting solutions were subjected to ^{1}H NMR spectroscopy at 298 K (Fig. S4). ^{1}H-NMR spectrum was recorded for each sample, and the peaks at 7.64, 7.53 and 7.40 ppm were monitored.

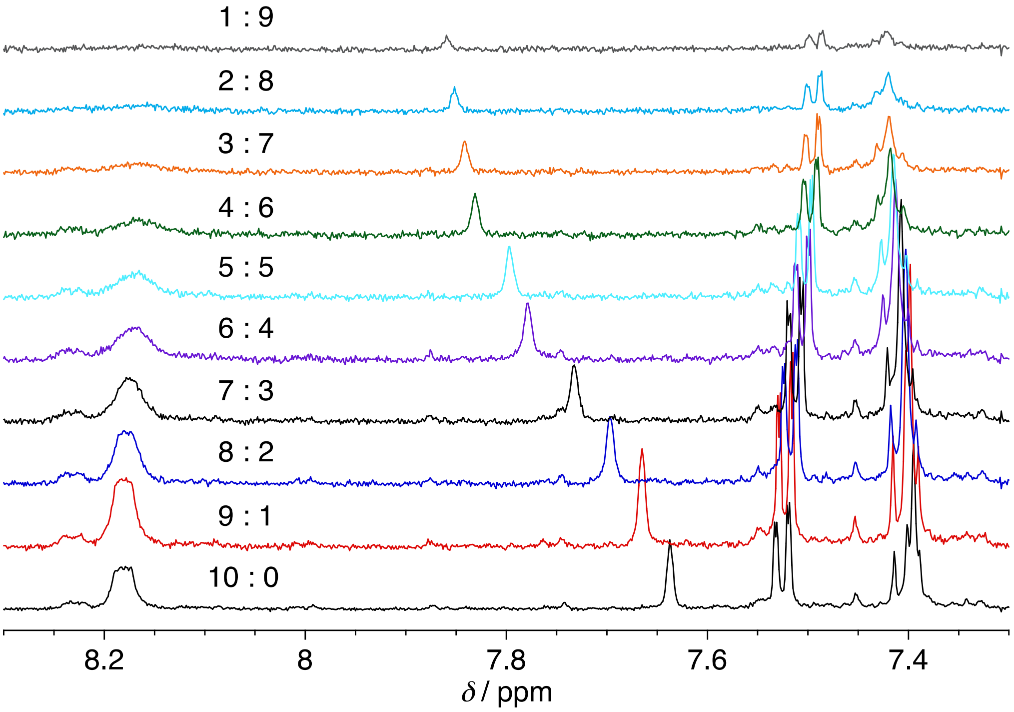

Fig. S4. ^{1}H NMR titration spectra of **N6** with C_{70} in toluene-d_8 at 298 K. [**N6**] : [C_{70}] = 10:0 to 1:9.

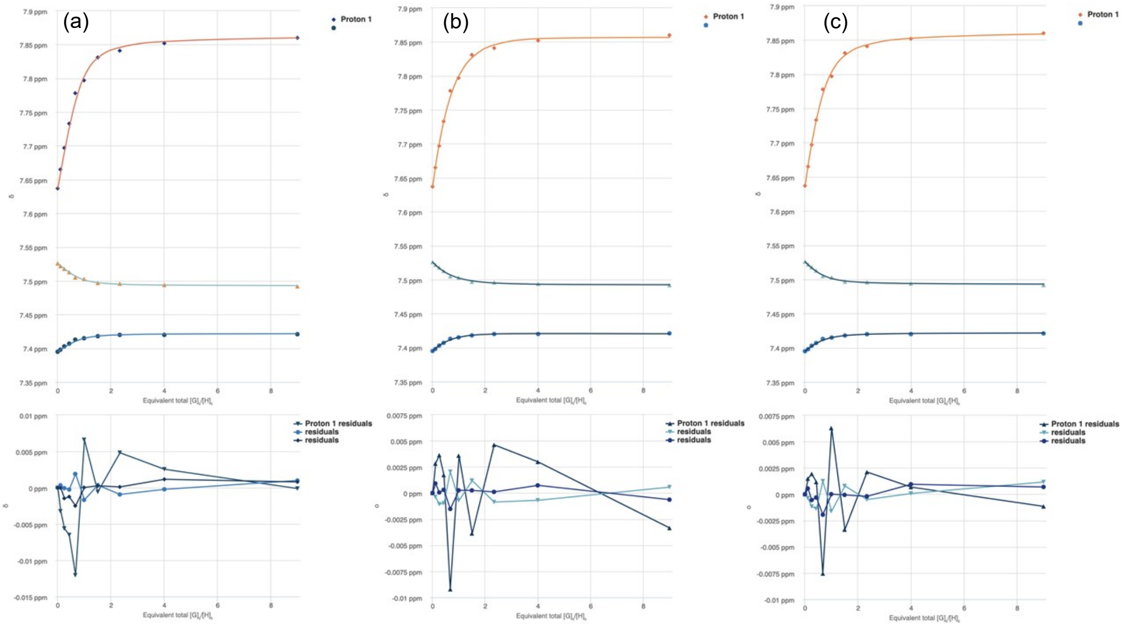

Fig. S5. Plots of chemical shift change of three different peaks (the initial data points: 7.64, 7.53 and 7.40 ppm, 10 samples, total data points $N = 30$) *versus* [C_{70}]/[**N6**]. Nonlinear curve regression of the titration of **N6** with C_{70} by using (a) 1:1 binding model, (b) 1:2 non-cooperative model, and (c) 2:1 additive model, associated with the Bindfit program.

Table S2. Different binding models for **N6** and C_{70} (the number of data points: $N = 30$)[S3]

Binding model	Relationship between		K_1 or K_{11} (M^{-1})	K_{12} or K_{21} (M^{-1})	k	SSR	AIC
	K_1 and K_2	$\delta_{\Delta HG2(or \Delta H2G)}$ and $2\delta_{\Delta HG}$					
1 : 1	K_1	$\delta_{\Delta HG}$	3.50×10^4 (±11%)	-	4	3.24×10^{-4}	–335
1:2 (full)	$K_1 \neq 4K_2$	$\delta_{\Delta HG2} \neq 2\delta_{\Delta HG}$	-	-	8	-	-
1:2 (noncooperative)	$K_1 = 4K_2$	$\delta_{\Delta HG2} \neq 2\delta_{\Delta HG}$	9.88×10^3 (±7.7%)	2.47×10^2 (±7.7%)	7	1.93×10^{-4}	–345
1:2 (additive)	$K_1 \neq 4K_2$	$\delta_{\Delta HG2} = 2\delta_{\Delta HG}$	-	-	5	-	-
1:2 (statistical)	$K_1 = 4K_2$	$\delta_{\Delta HG2} = 2\delta_{\Delta HG}$	-	-	4	-	-
2:1 (full)	$K_1 \neq 4K_2$	$\delta_{\Delta H2G} \neq 2\delta_{\Delta HG}$	5.75×10^4 (±23%)	1.02×10^4 (±68%)	8	1.12×10^{-4}	–359
2:1 (noncooperative)	$K_1 = 4K_2$	$\delta_{\Delta H2G} \neq 2\delta_{\Delta HG}$	-	-	7	-	-
2:1 (additive)	$K_1 \neq 4K_2$	$\delta_{\Delta H2G} = 2\delta_{\Delta HG}$	2.52×10^4 (±8.8%)	2.12×10^2 (±38%)	5	1.37×10^{-4}	–359
2:1 (statistical)	$K_1 = 4K_2$	$\delta_{\Delta H2G} = 2\delta_{\Delta HG}$	1.92×10^3 (±3.3%)	4.80×10^2 (±3.3%)	4	7.22×10^{-4}	–311

The $\delta_{\Delta HG}$, $\delta_{\Delta HG2}$ and $\delta_{\Delta H2G}$ denote the changes in the NMR resonances of interest upon forming a 1:1 ($\delta_{\Delta HG}$), 1:2 ($\delta_{\Delta HG2}$) and 2:1 ($\delta_{\Delta H2G}$) complex, respectively. K_{11}: the first stepwise association constant. K_{12} and K_{21}: the second stepwise association constants for 1:2 and 2:1 binding systems, respectively. Despite the same values of AIC, the size of errors for 2:1 additive model is much better than that of 2:1 full model.

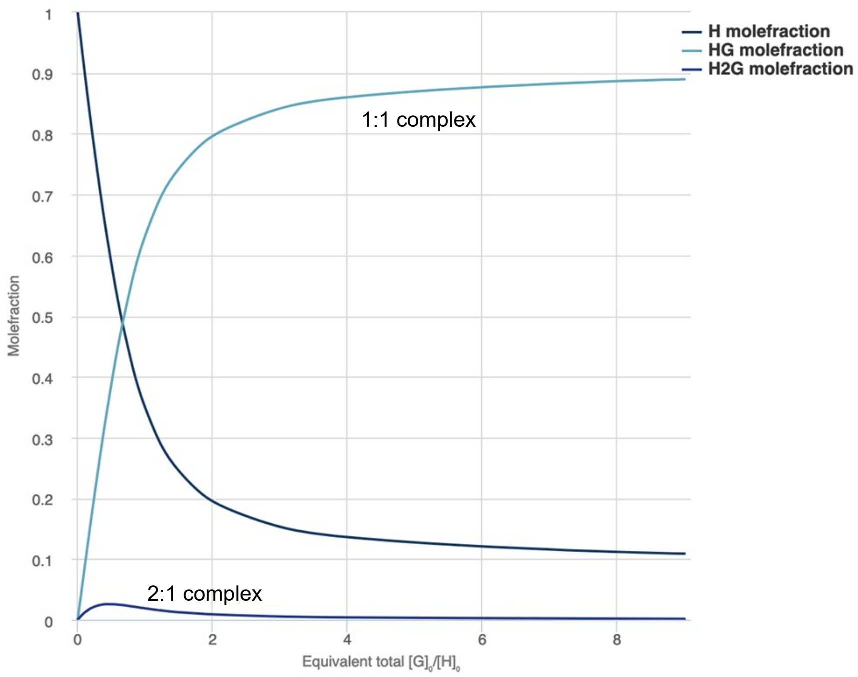

Fig. S6. Species evolution upon titration of C_{70} using the stoichiometric 2:1 additive binding model.[S7]

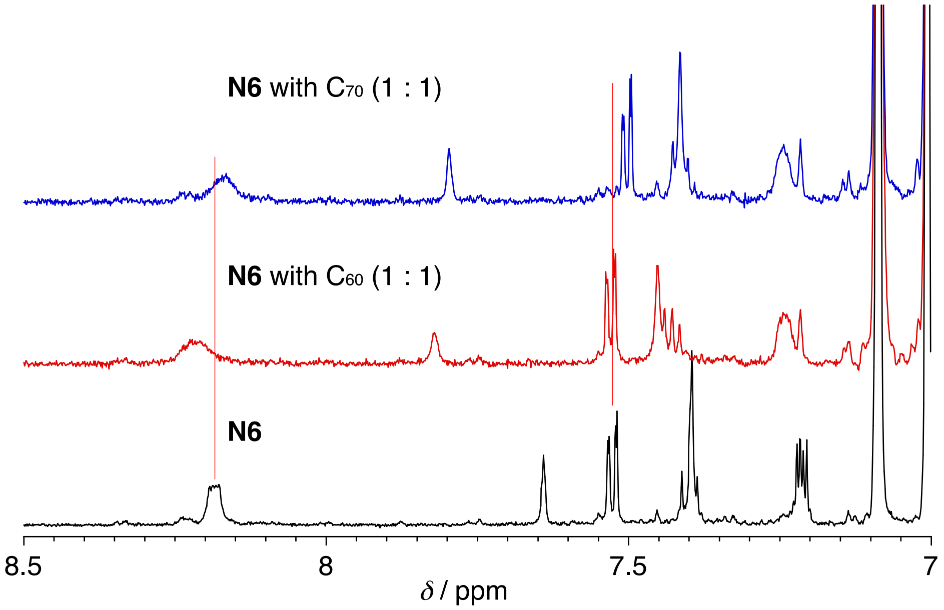

Fig. S7. ^{1}H NMR spectra of **N6** with and without fullerenes in toluene-d_8 at 298 K. The pink lines indicate the peaks where the addition of C_{60} and C_{70} shifts the peak in the opposite direction.

Table S1. Crystal data for C_{70}@**N6**

Single-crystals of **N6**-C_{70} composite were obtained by vapor diffusion of MeOH into a chlorobenzene solution of 1:1 mixture of **N6** and C_{70} in 4 ml vial.

Empirical formula	$C_{96}H_{60}·C_{70}·C_6H_5Cl$	
Formula weight	2166.69	
Temperature	103 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1 (#2)	
Unit cell dimensions	a = 11.75(4) Å	α = 106.46(3)°
	b = 14.98(5) Å	β = 101.62(3)°
	c = 15.88(5) Å	γ = 98.45(3)°
Volume	2563(14) $Å^3$	
Z	1	
Density (calculated)	1.404 g/cm^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	1114	
Crystal size	0.100 x 0.050 x 0.020 mm^3	
Theta range for data collection	1.651 to 19.995°	
Index ranges	$-10 \leq h \leq 11$, $-14 \leq k \leq 13$, $-15 \leq l \leq 11$	
Reflections collected	5549	
Independent reflections	4553 [R(int) = 0.2291]	
Completeness to theta = 19.995°	95.1%	
Max. and min. transmission	0.998 and 0.642	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4553 / 1029 / 1114	
Goodness-of-fit on F^2	1.084	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1092$, $wR_2 = 0.2259$	
R indices (all data)	$R_1 = 0.4092$, $wR_2 = 0.4205$	
Largest diff. peak and hole	0.255 and –0.332 e.$Å^{-3}$	

The structure of the fullerene at the special position was analyzed by applying appropriate DFIX, DANG and SIMU instructions.

Explanation for "level A" alerts: since the data crystal was tiny and contained disordered molecules, they gave only weak diffractions. However, these are not significant concern for the main skeletal structure.

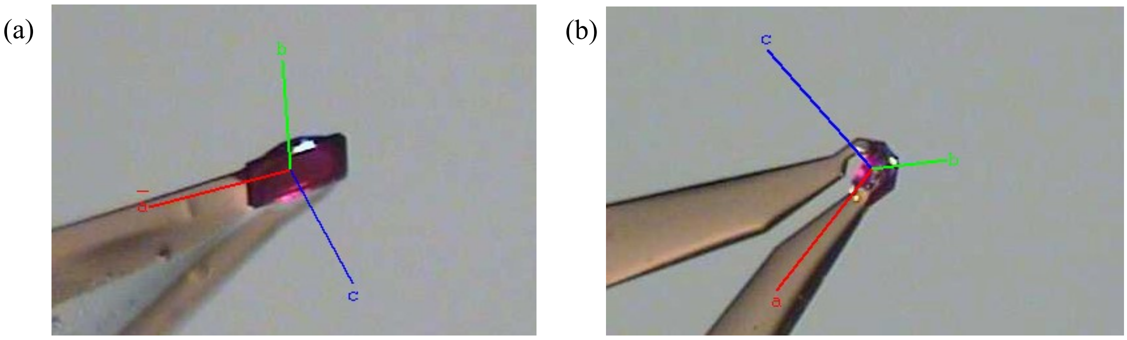

Fig. S8. The data crystals of (a) C_{60}@**N6** and (b) C_{70}@**N6**.

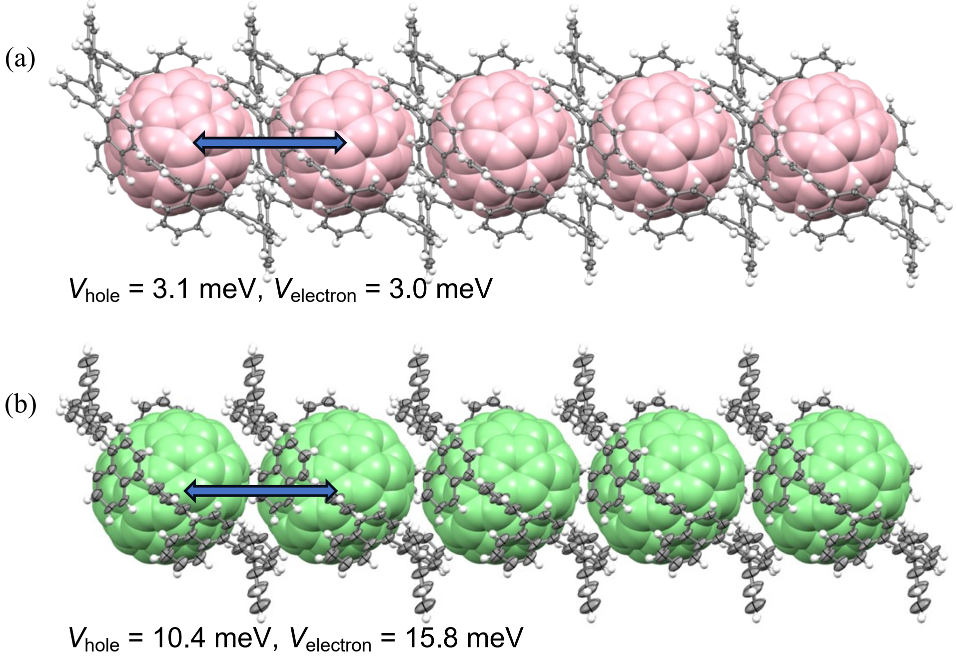

Fig. S9. Columnar arrays of (a) C_{60}[S8] and (b) C_{70} along the *a*-axis. Charge transfer integrals in the crystal packing structures were calculated using the ADF program[S9] at the PBE/TZ2P level of theory.

Reference

[S1] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv*., 2015, **A71**, 3–8.

[S2] G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem*., 2015, **C71**, 3–8.

[S3] Bindfit, http://supramolecular.org.

[S4] L. J. Farrugia, *J. Appl. Cryst*. **2012**, *45*, 849-854.

[S5] Mercury 4.0: from visualization to analysis, design and prediction, C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Cryst*., **2020**, *53*, 226-235.

[S6] K. Ikemoto, K. Takahashi, T. Ozawa and H. Isobe, *Angew. Chem., Int. Ed*. 2023, **62**, e202219059.

[S7] P. Thordarson, *Chem. Soc. Rev*. 2011, **40**, 1305-1323.

[S8] P. Mei, A. Matsumoto, H. Hayashi, M. Suzuki, N. Aratani, H. Yamada, *RSC. Adv*., 2018, **8**, 20872-20876.

[S9] ADF2021, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.