

Supramolecular assemblies of a nitro- gen-embedded buckybowl dimer with C₆₀

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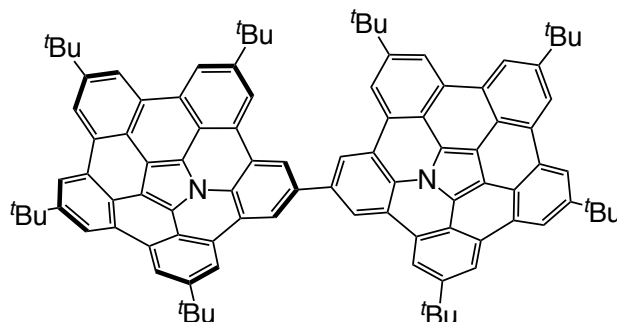
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Instrumentation and Materials

^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded using a Bruker AVANCE III HD spectrometer, and chemical shifts were reported as the delta scale in ppm relative to CHCl_3 ($\delta = 7.260$ ppm.), toluene- d_8 ($\delta = 7.000$ ppm.) for ^1H NMR and CDCl_3 ($\delta = 77.0$ ppm.) for ^{13}C NMR. Ultraviolet–visible–near infrared absorption spectra were measured in 1 cm quartz cell on a Shimadzu JASCO V670 spectrometer. Emission spectra were recorded using a JASCO FP-6500 spectrometer and absolute fluorescence quantum yields were measured by the photon counting method using an integration sphere. High-Resolution (HR) Mass spectrum was recorded on a Bruker micro TOF using positive mode ESI method for acetonitrile/ CH_2Cl_2 solutions. Cyclic voltammogram and differential-pulse voltammogram were recorded using an ALS electrochemical analyzer 612C. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. X-ray crystal diffraction data were taken on a Bruker D8 QUEST X-ray diffractometer equipped with PHOTON 100 CMOS active pixel sensor detector and ImS microfocus source using Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) or a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics using graphite monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71075$ Å). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis



Compound 2

A Schlenk tube containing compound **3** (50.0 mg, 55.4 μmol), K_2CO_3 (61.2 mg, 0.443 mmol), $\text{Pd}(\text{OAc})_2$ (2.45 mg, 10.9 μmol) and $[\text{HPCy}_3][\text{BF}_4]$ (8.14 mg, 22.1 μmol) were flushed with N_2 three times. To the tube, dry and degassed DMA (6.25 ml) was added. The mixture was stirred for 29 h at 130 $^\circ\text{C}$. The resulting mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was washed with water, dried over Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography (hexane/ CH_2Cl_2 = 85:15 v/v%) afforded compound **2** (11.2 mg, 8.50 μmol) in 31% yield as a yellow solid. ^1H NMR (500 MHz) (CDCl_3): δ = 8.68 (s, 2H), 8.62 (s, 2H), 8.58 (s, 2H), 8.56 (s, 2H), 8.42 (s, 2H), 1.65 (s, 18H), 1.64 (s, 18H) ppm.; ^{13}C NMR (126 MHz) (CDCl_3): δ = 148.96, 147.81, 140.20, 137.66, 134.66, 132.60, 131.30, 130.17, 129.39, 128.61, 127.66, 126.47, 123.28, 122.10, 120.86, 120.15, 119.44, 118.04, 36.02, 35.88, 32.32, 32.20 ppm.; ultraviolet–visible (CH_2Cl_2): λ_{max} (ϵ [$\text{M}^{-1}\text{cm}^{-1}$]) = 407 (91000), 456 (29000), 470 (26000), 494 (17000) nm; fluorescence (CH_2Cl_2 , λ_{ex} = 400 nm): λ_{em} = 519 and 551 nm (Φ_{f} = 0.17); high-resolution APCI–MS: m/z = 1321.7303, calcd for $(\text{C}_{100}\text{H}_{93}\text{N}_2)^+$ = 1321.7339 [$(\text{M}+\text{H})^+$].

^1H and ^{13}C NMR Spectra

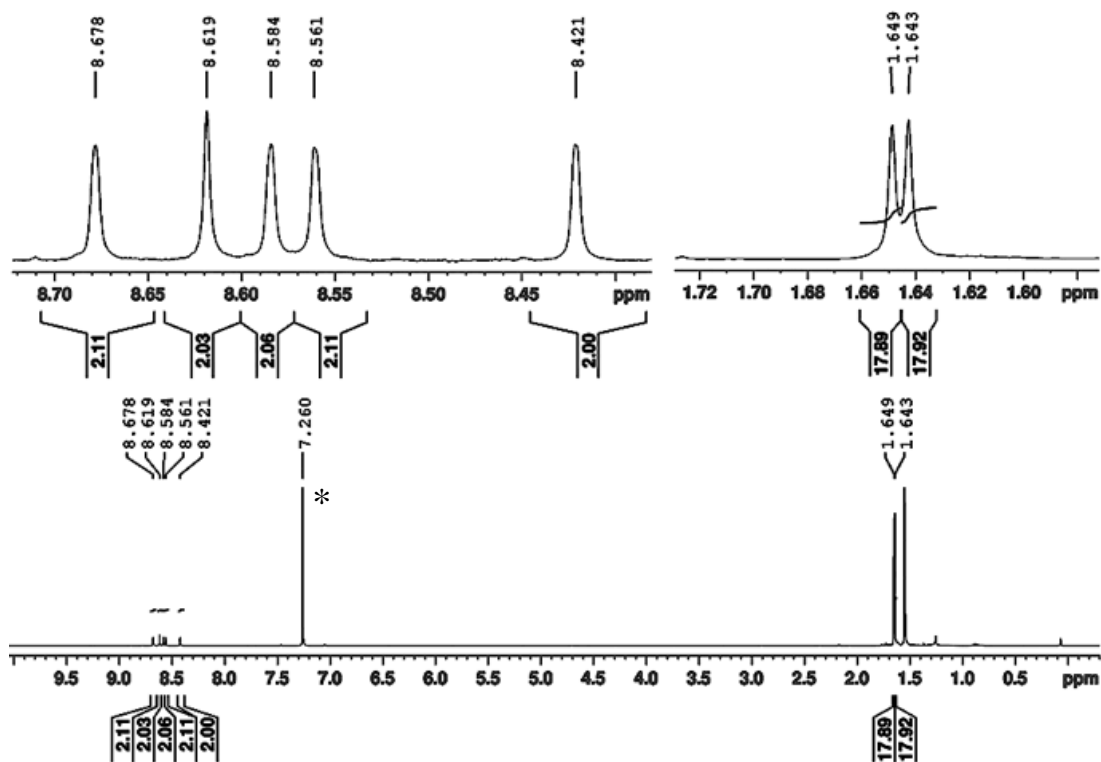


Fig. S1. ^1H NMR spectrum of **2** in CDCl_3 .

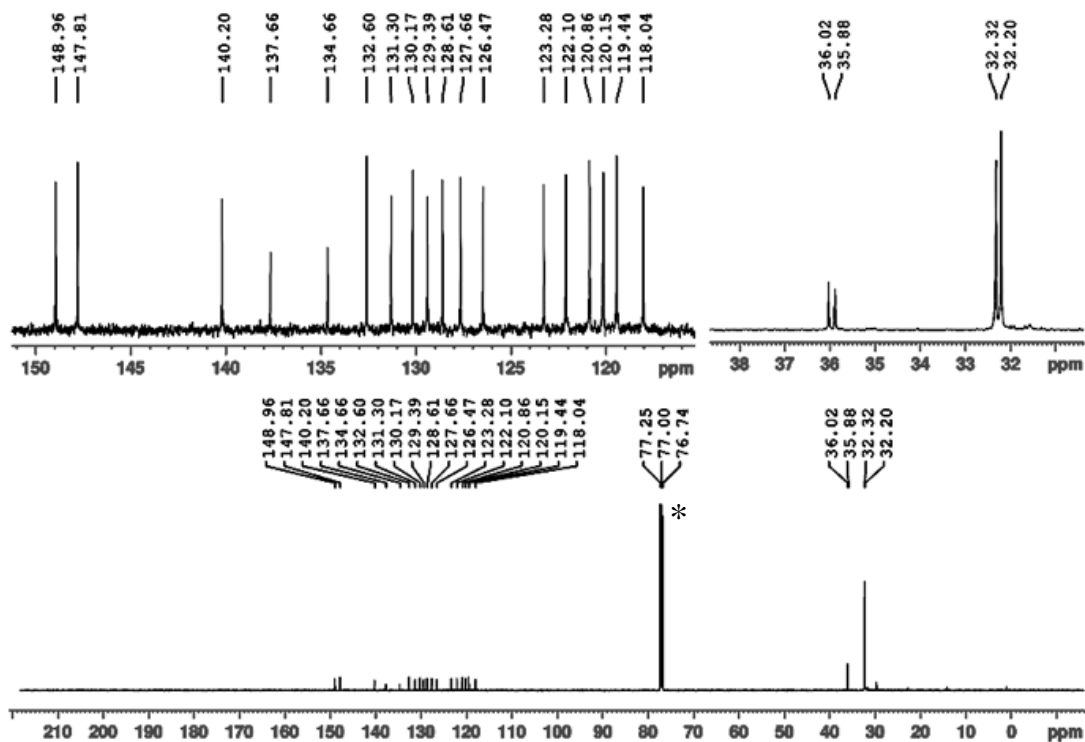


Fig. S2. ^{13}C NMR spectrum of **2** in CDCl_3 .

Electrochemical Analysis

Measurements were performed in freshly distilled dichloromethane with tetrabutylammonium hexafluorophosphate as electrolyte. A three electrodes system was used. The system consisted of a platinum working electrode, a platinum wire and Ag/AgClO₄ as the reference electrode. The scan rate was 100 mVs⁻¹. The measurement was performed under nitrogen atmosphere. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.

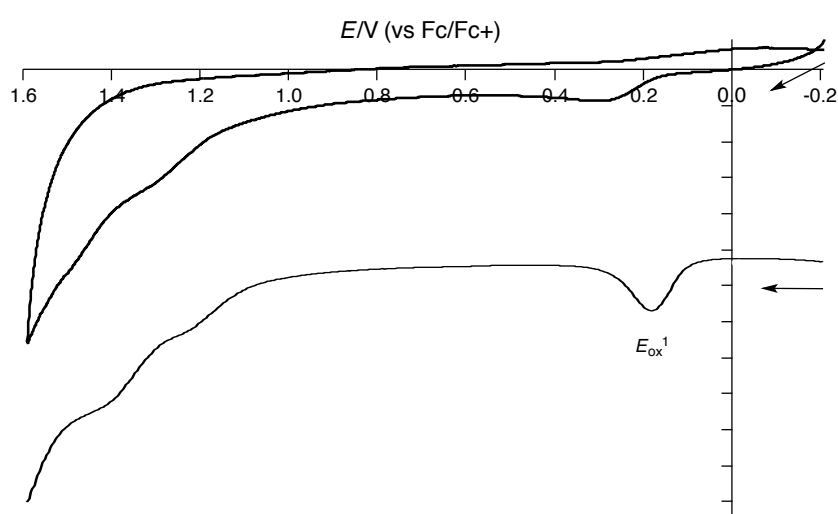


Fig. S3. Cyclic voltammograms (top) and differential pulse voltammograms (bottom) of **2** in CH₂Cl₂.

Titration experiments

Titration of **2** with C₆₀ in 1,2-dichlorobenzene or toluene

The binding constant (K_a) of C₆₀ with compound **2** was determined by UV/vis absorption spectra. The titrations were performed by the addition of a C₆₀ solution into the host solution. After the every addition, the mixture was stirred over 10 min to achieve the equilibrium state. The fitting was performed with the correlation between the change of absorbance (ΔA_{obs}) at 800 nm and the initial concentration of the guest $[G]_0$ using the equation as follows (1:1 binding model)¹:

$$\Delta A_{\text{obs}} = \epsilon \Delta_{\text{HG}} * \left\{ \frac{([G]_0 + [H]_0 + 1/K_a)}{2} - \sqrt{\left(\frac{([G]_0 + [H]_0 + 1/K_a)}{2} \right)^2 - 4 * [G]_0 * [H]_0} \right\}^{0.5}$$

K_a and $\epsilon \Delta_{\text{HG}}$ were optimized as parameters in the nonlinear curve fitting using Igor Pro 6.37 (Wavemetrics, Inc.). The titration experiments were carried out twice and the averaged K_a value of **2** was obtained. The values were $7.5 \times 10^3 \text{ M}^{-1}$ for the first attempt and $8.0 \times 10^3 \text{ M}^{-1}$ for the second attempt. The average K_a is $7.8 \times 10^3 \text{ M}^{-1}$.

Parameters and Variables:

$$\Delta A_{\text{obs}} = A_{\text{exp}} - A_0$$

ϵ_{HG} = molar extinction coefficient for the 1:1 complex

$[G]_0$ = the initial concentration of the guest

$[H]_0$ = the initial concentration of the host

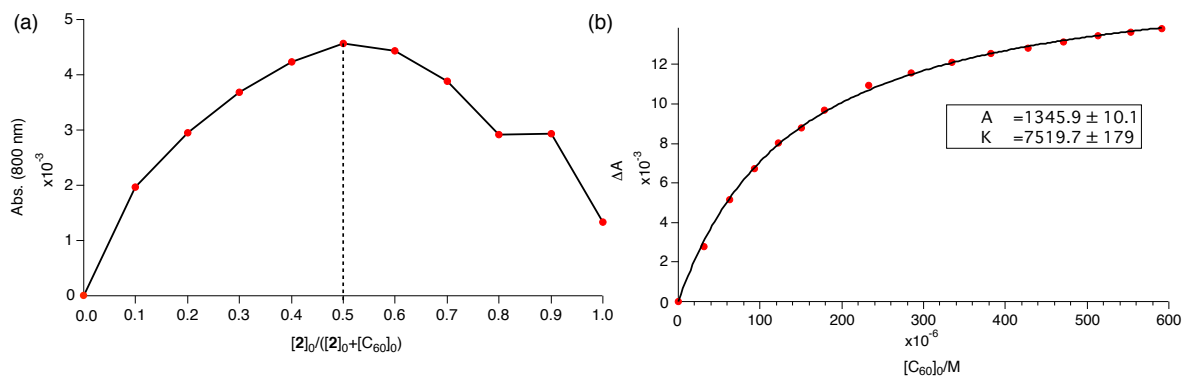


Fig. S4. (a) Job's plots for the complexation of **2** and C₆₀. (b) Nonlinear curve regression of the titration of **2** with C₆₀. All experiments were conducted in 1,2-dichlorobenzene.

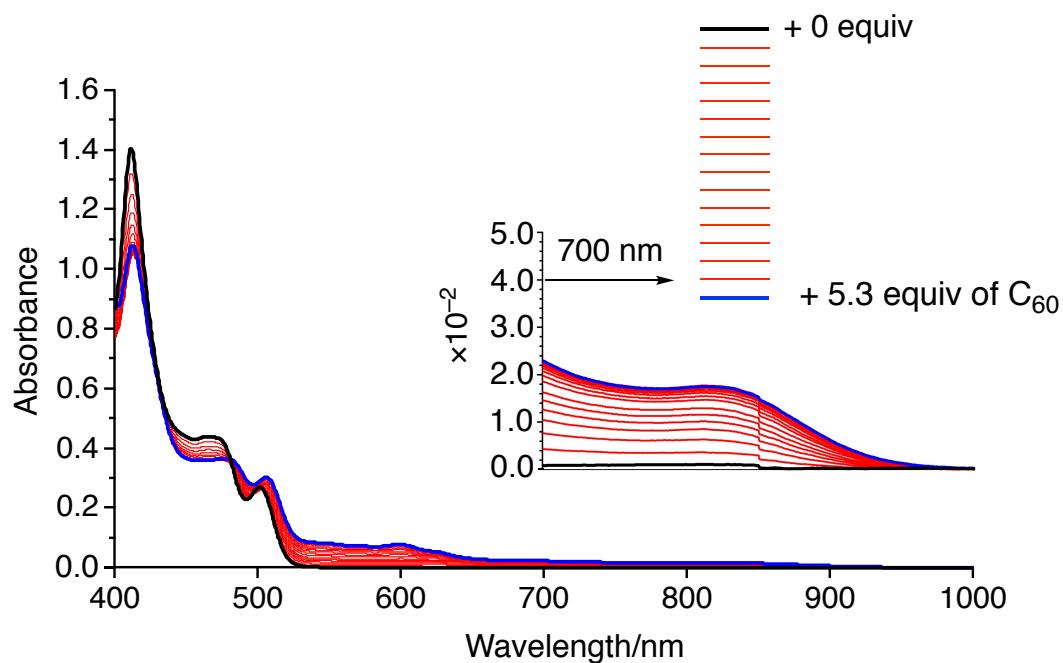


Fig. S5. UV-vis-NIR absorption spectra on addition of 0-5.3 equiv of C_{60} into a toluene solution of **2** ($c = 1.4 \times 10^{-5} \text{ M}^{-1}$). The estimated K_a values by UV-vis-NIR spectral analysis were $1.0 \times 10^5 \text{ M}^{-1}$ for both first and second attempts. The average K_a is $1.0 \times 10^5 \text{ M}^{-1}$.

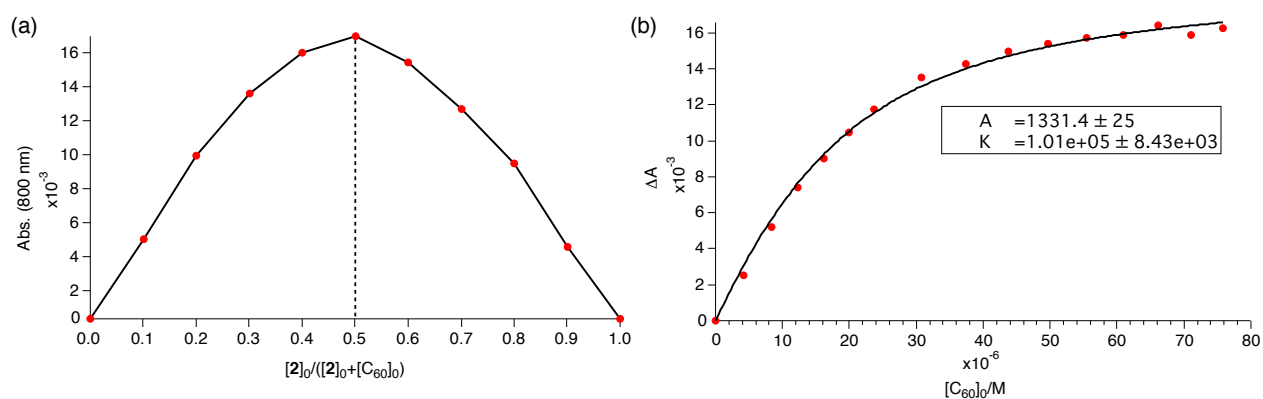


Fig. S6. (a) Job's plots for the complexation of **2** and C_{60} . (b) Nonlinear curve regression of the titration of **2** with C_{60} . All experiments were conducted in toluene.

X-Ray Structure

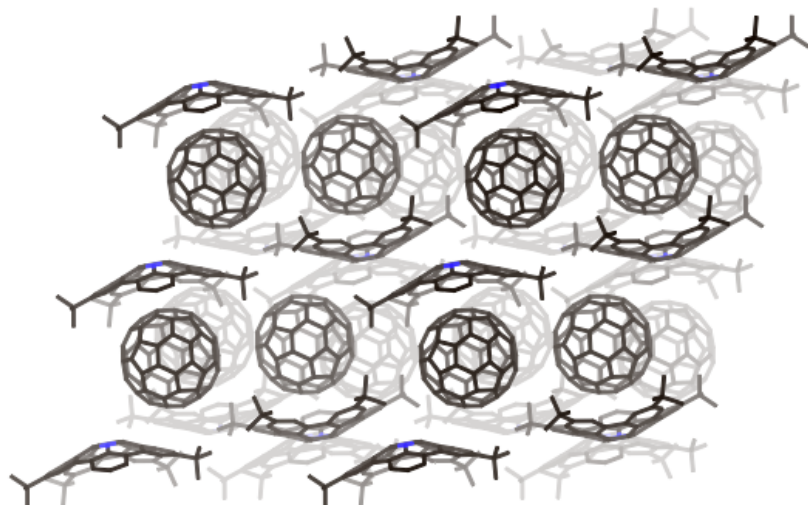


Fig. S7. The packing structure of the crystal of **1•C₆₀**. Solvent molecules (toluene) and hydrogen atoms in the crystal structure were omitted for clarity.

Time-Resolved Microwave Conductivity Measurement

Transient photoconductivity was measured by FP-TRMC. A resonant cavity was used to obtain a high degree of sensitivity in the conductivity measurement. The resonant frequency and microwave power were set at ~ 9.1 GHz and 3 mW, respectively, such that the electric field of the microwave was sufficiently small not to disturb the motion of charge carriers. The conductivity value is converted to the product of the quantum yield ϕ and the sum of charge-carrier mobilities $\Sigma\mu$ by $\phi\Sigma\mu = \Delta\sigma (eI_0F_{\text{light}})^{-1}$, where e , I_0 , F_{light} and $\Delta\sigma$ are the unit charge of a single electron, incident photon density of excitation laser (photons per m^2), a correction (or filling) factor (m^{-1}) and a transient photoconductivity, respectively. The sample was set at the highest electric field in a resonant cavity. FP-TRMC experiments were performed at room temperature. The measurements of **2** and **2**• C_{60} were performed for powder and crystalline samples respectively. These samples were covered with a PVA film on a quartz substrate.

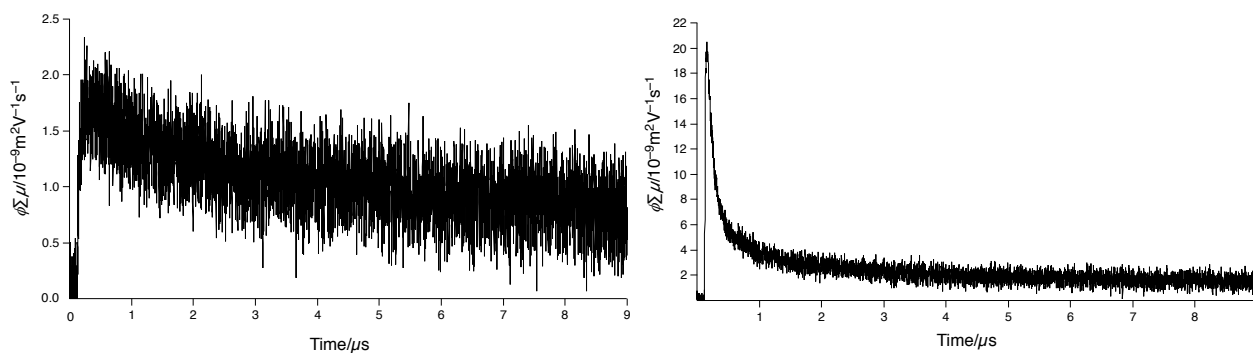


Fig. S8. Kinetic traces of a photoconductivity transient of **2** and the crystal of **2**• C_{60} by FP-TRMC method.

DOSY Measurements

The diffusion coefficients (D) of **1**, **2**, **1**+ C_{60} , and **2**+ C_{60} were determined by ^1H NMR measurement at the concentrations of 0.8 mM. The mixture of host and C_{60} were dissolved in toluene- d_8 , and then stirred over 10 min to achieve the equilibrium state. All experiments were conducted at 20 °C.

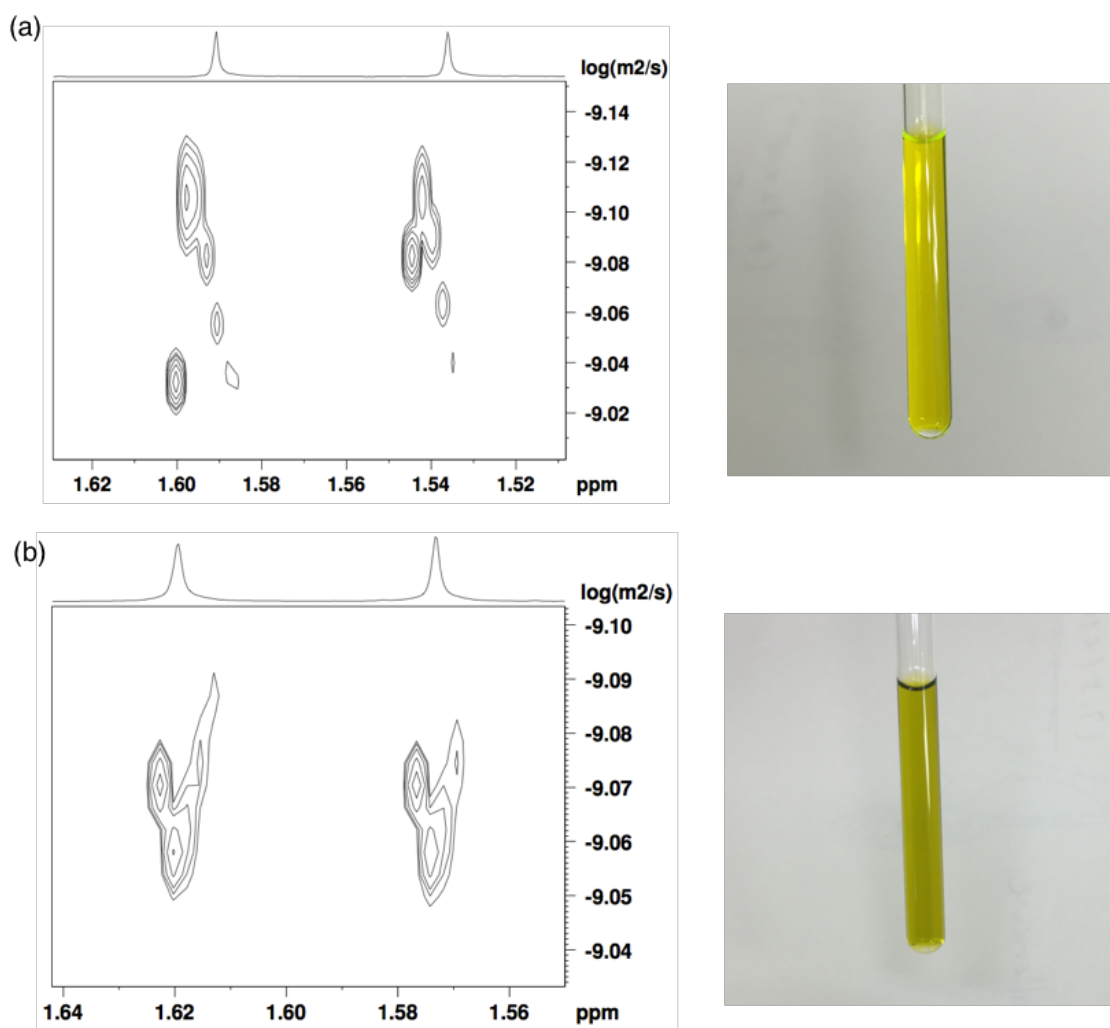


Fig. S9. The DOSY measurements of (a) **1** and (b) **1**+0.5 equiv of C_{60} in d_8 -toluene. The images of the samples were shown to the right of each spectrum. The diffusion coefficient (D) of **1** was $8.74 \times 10^{-10} \text{ m}^2/\text{s}$, and the value was $8.54 \times 10^{-10} \text{ m}^2/\text{s}$ in the presence of 0.5 equiv of C_{60} .

SEM Measurements

Field emission scanning electron microscopy (FE-SEM) samples were prepared by drop-cast of toluene solution of **1**, **1**+C₆₀, **2** and **2**+C₆₀ on silicon wafer. The images were recorded on a JEOL JSM-7500F microscope with the accelerating voltages of 1 kV for **1**, **2**, and 2 kV for **1**+C₆₀, **2**+C₆₀.

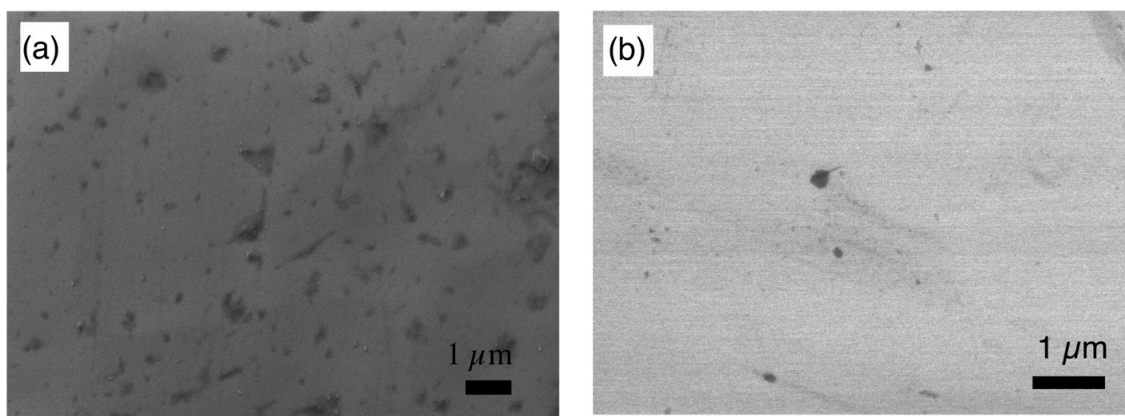


Fig. S10. The SEM images of (a) **1** and (b) **1** with 1.0 equiv of C₆₀.

NMR Measurements Using Internal Standard

We prepared the **solution A** and **B** respectively as follows and then 0.50 mL of **Solution A** and 0.30 mL of **solution B** were mixed, which was used in NMR measurement.

Solution A: The mixture of **2** (2.18 mg, 1.65 μmol) and 1,1,2,2-tetrachloroethane (1.60 mg, 9.53 μmol) in 2.0 mL of toluene- d_8 .

Solution B: C₆₀ (1.00 mg, 1.39 μmol) in 2.0 mL of toluene- d_8 .

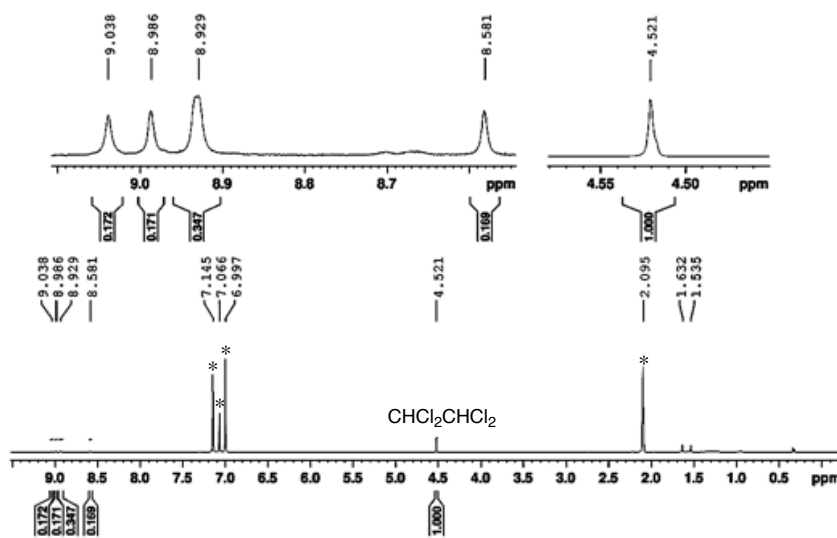


Fig. S11. ¹H NMR spectrum of **2**+C₆₀ (0.5 equiv) in toluene- d_8 at -40 °C. 1,1,2,2-tetrachloroethane was used as the internal standard.

NMR Measurements Using C₆₀

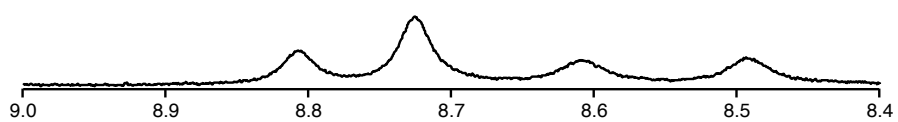


Fig. S12 The ¹H NMR spectra of **2** (0.52 mM) with 2.0 equiv of C₆₀ at r.t.

XRD measurements

The measurements of **2** and **2**•C₆₀ crystal were performed for powder and crystalline samples respectively. The sample of **2**•C₆₀ fibre was prepared by drop-cast of toluene solution of the mixture of **2** and 1 equiv of C₆₀ on silicon wafer. X-ray diffraction data of **2**, **2**+C₆₀ crystal and **2**+C₆₀ fibre were taken on a X-ray diffractometer Rigaku FR-E equipped with two-dimensional detector Rigaku R-axis IV using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$)

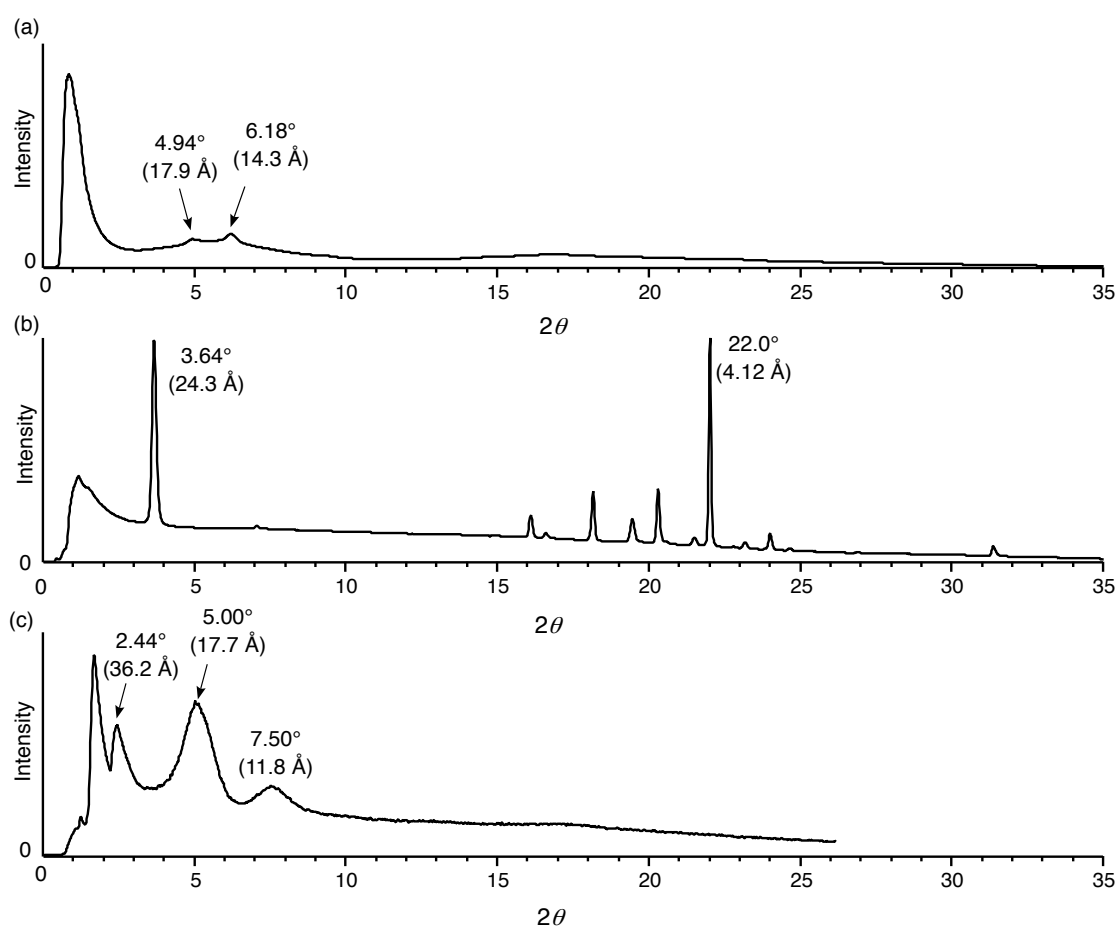


Fig. S13. The XRD spectra of (a) **2**, (b) **2**•C₆₀ crystal and (c) **2**•C₆₀ fibre.

Table S1. Peak list details of XRD pattern of **2**, **2**•C₆₀ crystal and **2**•C₆₀ fibre

Compound	Angle 2θ	d-value (Å)
2	4.94	17.9
2 +C ₆₀ crystal	3.64	24.3
	7.04	12.6
	16.08	5.51
	16.58	5.35
	18.14	4.92
	19.44	4.57
	20.3	4.37
	21.5	4.13
	22.0	4.04
	23.16	3.84
	23.98	3.71
	24.64	3.61
31.36	2.85	
2 +C ₆₀ fibre	2.44	36.2
	5.00	17.7
	7.50	11.8

Theoretical Calculations

All calculations were carried out using the Gaussian 09 program.² The simulated absorption spectra of 1:1 and 2:1 complexes were obtained by the TD-DFT method at the B3LYP/6-31G(d) level using X-ray crystal structures without any structural optimization. The estimated structure of the 1D chain-like supramolecular assembly was calculated by PM6 semi-empirical calculations.

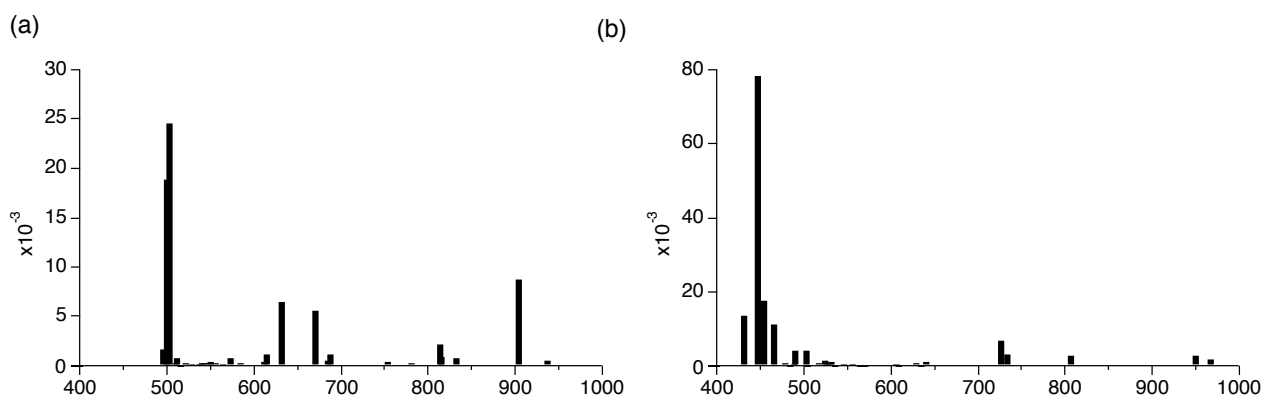


Fig. S14. The simulated theoretical absorption bands and oscillator strengths of (a) a 2:1 complex between **1** and C₆₀ (b) a 1:1 complex between **1** and C₆₀.

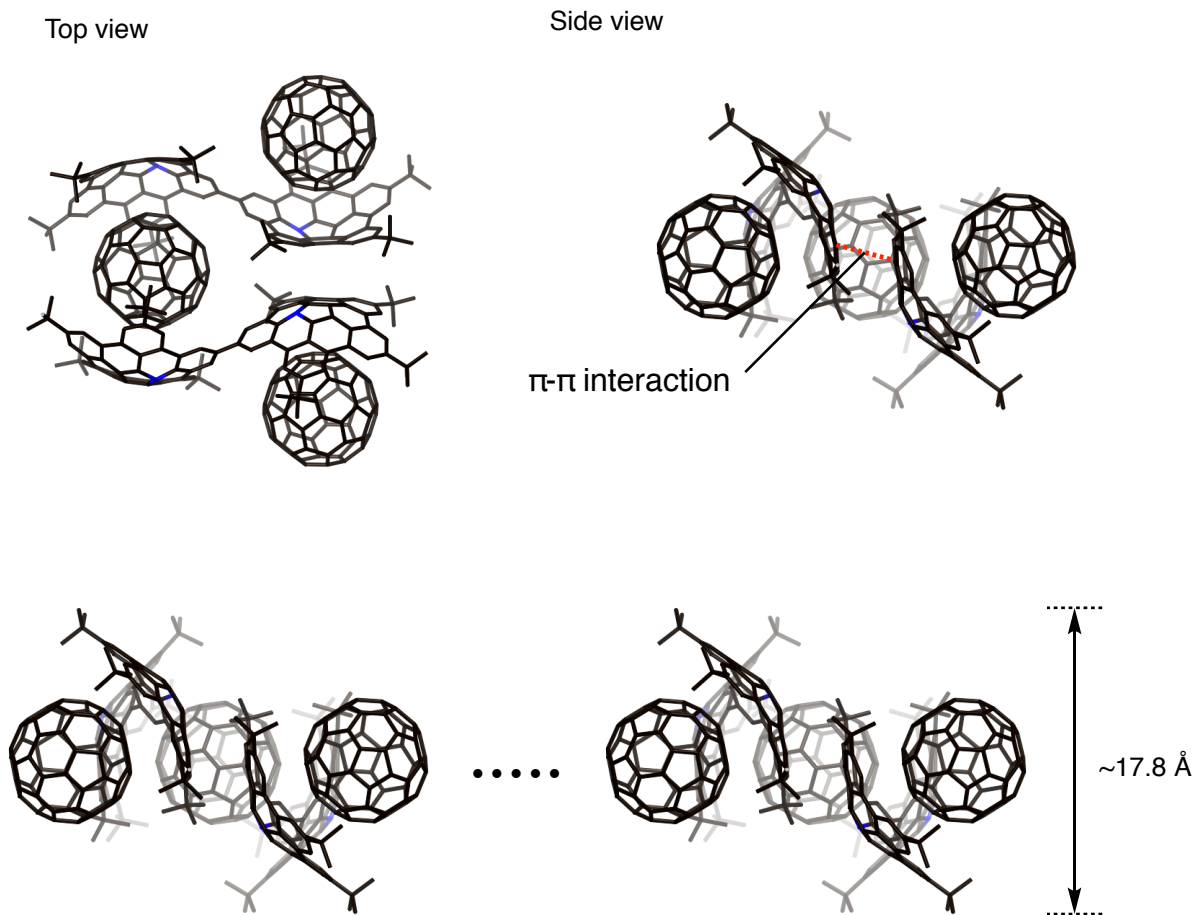


Fig. S15. The optimized structure of the 1D chain-like supramolecular assembly at the PM6 level.

References

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- [2] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.