Electronic Supplementary Information

Synthesis of Pentadecaphenylenes, Its Inclusion Properties, and Nanostructure Formation with C_{60}

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Contents

S1. Materials and methods

NMR spectra were recorded on Bruker Biospin 500 (500 MHz ^{1}H NMR and 125 MHz ^{13}C NMR) spectrometers using tetramethylsilane as the internal standard. UV-Vis spectra were recorded on SHIMADZU UV-3101PC UV-VIS-NIR Scanning Spectrophotometer and ILF-533 integrated share with UV Probe application. Fluorescence emissions were recorded on JASC FP-6500 Spectrofluorometer and ISR-3100 integrated share. Mass spectra were recorded with SHIMADZU GCMS-QP2010 spectrometer and KRATOS AXIMA-CFR spectrometer with Kompact MFC application. XRD pattern was measured with a RINT-TTRIII diffraction meter with Cu-Kα radiation (50 kV, 300 mA). Elemental analyses were performed in the micro analysis laboratory of Tokyo Metropolitan University. DFT calculations were performed with the Gaussian 09 program. All geometry optimizations were carried out at the B3LYP/6–31G(d) basis set. For **1c**, the optimized structure with C_3 symmetry was found to be the minimum. Thin layer chromatography (TLC) was performed with Merck 60 F_{254} silica gel pre-coated plates. Column chromatography was performed with Daisogel IR-60 (60/210nm). Melting Points were determined with Yanaco MP-500D melting point apparatus. The solvents used for synthesis were dried and purified by usual techniques prior to use.

S2. 4-(Trimethylsilyl)biphenylboronic acid (3)

To a solution of 4-bromo-4′-(trimethylsilyl)biphenyl (6.12 g, 20.0 mmol) in dry THF (200 ml) was added dropwise a hexane solution of *n*-BuLi (8.5 ml, 22.1 mmol, 2.6M in hexane) at −78 °C under nitrogen atmosphere. After stirring the mixture at the same temperature for 1 h, trimethoxyborane (6.6 ml, 60 mmol) was added dropwise. The reaction mixture was allowed to warm up to room temperature with continuous stirring. After stirring for 16 h, aq. 2M HCl was added and stirred for another 1 h. The aqueous layer was extracted with dichloromethane and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* to give **3** (5.20 g) which was used without further purification.

S3. 4,4′′′′-Bis(trimethylsilyl)-4′′,5′′-dioctyl-1,1′:4′,1′′:2′′,1′′′:4′′′,1′′′′-quinquephenyl (4a)

To a deoxygenated solution of 4-(trimethylsilyl)biphenylboronic acid **3** (5.20 g, 19.3 mmol) and K_2CO_3 (9.48 g, 68.6 mmol) in water (35 ml) and ethanol (90 ml) were added a deoxygenated solution of 1,2-diiodo-4,5-dioctylbenzene (3.612 g, 6.5 mmol) in toluene (130 ml) and $Pd^0(PPh_3)_4$ (758 mg, 10 mol%) under nitrogen atmosphere. The resulting mixture was heated under reflux for 4 h. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with water and dried over anhydrous $MgSO_4$. After removal the solvent *in vacuo*, the residue was column chromatographed on silica gel using hexane/benzene (v/v 6:1) as eluent to afford 3.617 g (74%) of **4a** as white solid (m.p. 57–58 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.57 (s, 8H), 7.47 (d, J = 8.0 Hz, 4H), 7.27 (s, 2H), 7.24 (d, J = 8.0 Hz, 4H), 2.69 (t, J = 8.0 Hz, 4H), 1.69−1.63 (m, 4H), 1.47−1.42 (m, 4H), 1.40−1.22 (m, 16H), 0.88 (t, J = 7.5 Hz, 6H), 0.28 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 141.1, 140.7, 140.1, 139.0, 138.8, 137.3, 133.8, 131.5, 130.3, 126.5, 126.2, 32.5, 31.9, 31.4, 29.9, 29.5, 29.3, 22.7, 14.1, −1.1; LDI-TOF MS: *m/z* 750 (M^+); Anal. for $C_{52}H_{70}Si_2$: calcd. C, 83.13; H, 9.39. Found C, 83.93; H, 9.52.

S4. 4,4′′′′-Bis(trimethylsilyl)-4′′,5′′-dibutyl-1,1′:4′,1′′:2′′,1′′′:4′′′,1′′′′-quinquephenyl (4b)

To a deoxygenated solution of 4-(trimethylsilyl)biphenylboronic acid **3** (6.46 g, 23.9 mmol) and K_2CO_3 (11.62 g, 84 mmol) in water (45 ml) and ethanol (120 ml) were added a deoxygenated solution of 1,2-diiodo-4,5-dibutylbenzene (3.992 g, 9.0 mmol) in toluene (160 ml) and $Pd^0(PPh_3)_4$ (1.038 g, 10 mol%) under nitrogen atmosphere. The resulting mixture was heated under reflux for 4 h. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with water and dried over anhydrous $MgSO_4$. After removal the solvent *in vacuo*, the residue was column chromatographed on silica gel using hexane/benzene (v/v 6:1) to afford 3.566 g (62%) of **4b** as white solid (m.p. 188–189 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.57 (s, 8H), 7.47 (d, J = 8.0 Hz, 4H), 7.27 (s, 2H), 7.24 (d, J = 8.0 Hz, 4H), 2.71 (t, J = 8.0 Hz, 4H), 1.69−1.63 (m, 4H), 1.50−1.43 (m, 4H), 0.99 (t, J = 7.5 Hz, 6H), 0.29 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 141.1, 140.7, 140.1, 139.1, 138.8, 137.4, 133.8, 131.5, 130.3, 126.5, 126.2, 33.6, 32.2, 23.0, 14.1, −1.1; LDI-TOF MS: *m/z* 638 (M^+); Anal. for $C_{44}H_{54}Si_2$: calcd. C, 82.69; H, 8.52. Found C, 82.40; H, 8.38.

S5. 4,4′′′′-Dibromo-4′′,5′′-dioctyl-1,1′:4′,1′′:2′′,1′′′:4′′′,1′′′′-quinquephenyl (5a)

To a stirred solution of **4a** (2.874 g, 3.83 mmol) in acetone (50 ml) was added *N*-bromosuccinimide (1.508 g, 8.5 mmol) in one portion at room temperature, and the resulting mixture was stirred for 20 h. After removing the solvent *in vacuo*, the residue was column chromatographed on silica gel using hexane/benzene (v/v 6:1) as eluent to afford 2.831 g (96%) of **5a** as white solid (m.p. 71–72 °C); ^{1}H NMR (CD_2Cl_2, 500 MHz): δ (ppm) 7.55 (d, J = 8.6 Hz, 4H), 7.48 (d, J = 8.6 Hz, 4H), 7.46 (d, J = 8.5 Hz, 4H), 7.26 (d, J = 8.5 Hz, 4H), 7.25 (s, 2H), 2.70 (t, J = 8.0 Hz, 4H), 1.69−1.62 (m, 4H), 1.46−1.40 (m, 4H), 1.38−1.25 (m, 16H), 0.89 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 141.1, 140.3, 139.7, 137.7, 137.1, 131.8, 131.5, 130.4, 128.5, 126.4, 121.4, 32.5, 31.9, 31.4, 29.9, 29.5, 29.3, 22.7, 14.1; MS (EI): *m/z* 764 (M^+); Anal. for $C_{46}H_{52}Br_2$: calcd. C, 72.25; H, 6.85. Found C, 72.51; H, 6.84.

S6. 4,4′′′′-Dibromo-4′′,5′′-dibutyl-1,1′:4′,1′′:2′′,1′′′:4′′′,1′′′′-quinquephenyl (5b)

To a stirred solution of **4b** (2.704 g, 4.23 mmol) in a mixed solvent of acetone (25 ml) and dichloromethane (15 ml) was added *N*-bromosuccinimide (1.657 g, 9.3 mmol) in one portion at room temperature, and the resulting mixture was stirred for 20 h. After removing the solvent *in vacuo*, the residue was column chromatographed on silica gel eluting hexane/benzene (v/v 6:1) to afford 2.347 g (85%) of **5b** as white solid (m.p. 114–115 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.53 (d, J = 8.6 Hz, 4H), 7.45 (d, J = 8.6 Hz, 4H), 7.43 (d, J = 8.5 Hz, 4H), 7.26 (s, 2H), 7.25 (d, J = 8.5 Hz, 4H), 2.70 (t, J = 8.0 Hz, 4H), 1.69–1.63 (m, 4H), 1.49–1.43 (m, 4H), 0.98 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 141.1, 140.3, 139.7, 137.7, 137.1, 131.8, 131.5, 130.4, 128.5, 126.4, 121.4, 33.5, 32.2, 22.9, 14.0; MS (EI): *m/z* 652 (M^+); Anal. for $C_{38}H_{36}Br_2$: calcd. C, 69.95; H, 5.56. Found C, 70.10; H, 5.52.

S7. 4,4′′′′-Diiodo-4′′,5′′-dioctyl-1,1′:4′,1′′:2′′,1′′′:4′′′,1′′′′-quinquephenyl (5c)

To a solution of **4a** (350 mg, 0.47 mmol) in carbon tetrachloride (20 ml) was added dropwise a CH_2Cl_2 solution of iodine monochloride (1.0 ml, 1.0 mmol, 1.0 M in CH_2Cl_2) at –20 °C under nitrogen atmosphere. After the addition, the reaction mixture was allowed to warm up to room temperature and stirred for another 2 h to complete the reaction. A saturated solution of $Na_2S_2O_3$ was added to remove unreacted ICl. The organic layer was separated, and the aqueous layer was extracted with CCl_4. The combined organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was column chromatographed on silica gel using hexane/benzene (v/v 6:1) as eluent to afford 349 mg (87%) of **5c** (m.p. 89–90 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.73 (d, J = 8.5 Hz, 4H), 7.43 (d, J = 8.0 Hz, 4H), 7.32 (d, J = 8.5 Hz, 4H) 7.25 (s, 2H), 7.24 (d, J = 8.0 Hz, 4H), 2.69 (t, J = 7.5 Hz, 4H), 1.69–1.63 (m, 4H), 1.46–1.40 (m, 4H), 1.38–1.24 (m, 16H), 0.89 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 141.1, 140.30, 140.20, 137.76, 137.70, 137.1, 131.5, 130.4, 128.7, 126.3, 92.8, 32.5, 31.9, 31.4, 29.9, 29.5, 29.3, 22.7, 14.1; MS (EI): *m/z* 858 (M^+); Anal. for $C_{46}H_{52}I_2$: calcd. C, 64.34; H, 6.10. Found C, 64.63; H, 6.19.

S8. Hexaoctylpentadecaphenylene (1a)

(i) To a solution of **5a** (615 mg, 0.80 mmol) in anhydrous THF (80 ml) was added dropwise a *t*-BuLi (2.1 ml, 3.34 mmol, 1.59 M in pentane) at –80 °C under nitrogen atmosphere. The mixture was stirred at the same temperature for 1.5 h, and CuCN (72 mg, 0.8 mmol) was added. The reaction mixture was allowed to warm up to –5 °C with vigorous stirring when all the CuCN was got dissolved in the solution. Duroquinone (394 mg, 2.40 mmol) was added in one portion at –5 °C, and the mixture was allowed to stand at room temperature with continuous stirring. It was stirred for another 3 h to complete the reaction. Water was added followed by the addition of dichloromethane. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was column chromatographed on silica gel using carbon disulfide / dichloromethane (v/v 19:1) as eluent to afford 135 mg (28%) of **1a** as white solid (m.p. 199–201 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.68 (s, 24H), 7.51(d, J = 9.0Hz, 12H), 7.32 (s, 6H), 7.21 (d , J = 9.0 Hz, 12H), 2.70 (t, J = 8.0Hz, 12H), 1.72–1.60 (m, 12H), 1.50–1.22 (m, 60H), 0.90 (t, J = 7.0 Hz, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 140.8, 140.2, 139.5, 139.3, 138.0, 137.6, 131.0, 130.5, 127.2, 126.2, 32.5, 31.9, 31.4, 30.0, 29.5, 29.3, 22.7, 14.1; UV-Vis (THF): λ_{max} (log ε) 318 (5.27) nm; LDI-TOF MS: *m/z* 1814.13 (M^+); Anal. for $C_{138}H_{156}$: calcd. C, 91.34; H, 8.66; Found C, 91.12; H, 8.44.

(ii) To a solution of **5c** (170 mg, 0.20 mmol) in anhydrous ether (25 ml) was added dropwise a *t*-BuLi (0.5 ml, 0.80 mmol, 1.59 M in pentane) at –80 °C under nitrogen atmosphere. The mixture was stirred at the same temperature for 1.5 h, and then CuCN (18 mg, 0.20 mmol) was added. The reaction mixture was allowed to warm up to –20 °C with vigorous stirring. It was stirred for 30 min within the temperature –20 to –15 °C when all the CuCN was got dissolved in the solution. Duroquinone (98 mg, 0.60 mmol) was added in one portion at –15 °C, and the mixture was stirred for 1 h at the same temperature. The mixture was allowed to stand at room temperature and stirred for 3 h to complete the reaction. Water was added followed by the addition of benzene. The organic layer was separated and the aqueous layer was extracted with benzene. The combined organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was column chromatographed on silica gel using carbon disulfide / dichloromethane (v/v 19:1) as eluent to afford 24 mg (20%) of **1a**.

S9. Hexabutylpentadecaphenylene (1b)

To a solution of **5b** (654 mg, 1.00 mmol) in anhydrous THF (100 ml) was added *t*-BuLi (2.8 ml, 4.45 mmol, 1.59 M in pentane) at –80 °C under nitrogen atmosphere. The mixture was stirred at the same temperature for 1.5 h and then CuCN (95 mg, 1.05 mmol) was added. The reaction mixture was allowed to warm up to –5 °C with vigorous stirring when all the CuCN was got dissolved in the solution. Duroquinone (494 mg, 3.01 mmol) was added in one portion at –5 °C, and the mixture was allowed to stand at temperature with continuous stirring. It was stirred for another 3 h to complete the reaction. Water was added followed by the addition of dichloromethane. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was column chromatographed on silica gel using carbon disulfide / dichloromethane (v/v 19:1) as eluent to afford 148 mg (30%) of **1b** as white solid (m.p. >295 °C decomp.); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.68 (s, 24H), 7.52(d, J = 8.2Hz, 12H), 7.32 (s, 6H), 7.23 (d , J = 8.2 Hz, 12H), 2.73 (t, J = 7.9Hz, 12H), 1.72–1.64 (m, 12H), 1.50–1.45 (m, 12H), 1.00 (t, J = 7.4 Hz, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 140.8, 140.1, 139.5, 139.3, 138.1, 137.6, 131.0, 130.5, 127.2, 126.2, 33.5, 32.2, 23.0, 14.1; UV-Vis (THF): λ_{max} (log ε) 318 (5.29) nm; LDI-TOF MS: *m/z* 1478.3 (M^+); Anal. for $C_{114}H_{108}$: calcd. C, 92.64; H, 7.36; Found C, 92.47; H, 7.45

S10. ^{1}H NMR spectrum of 4a (500 MHz)

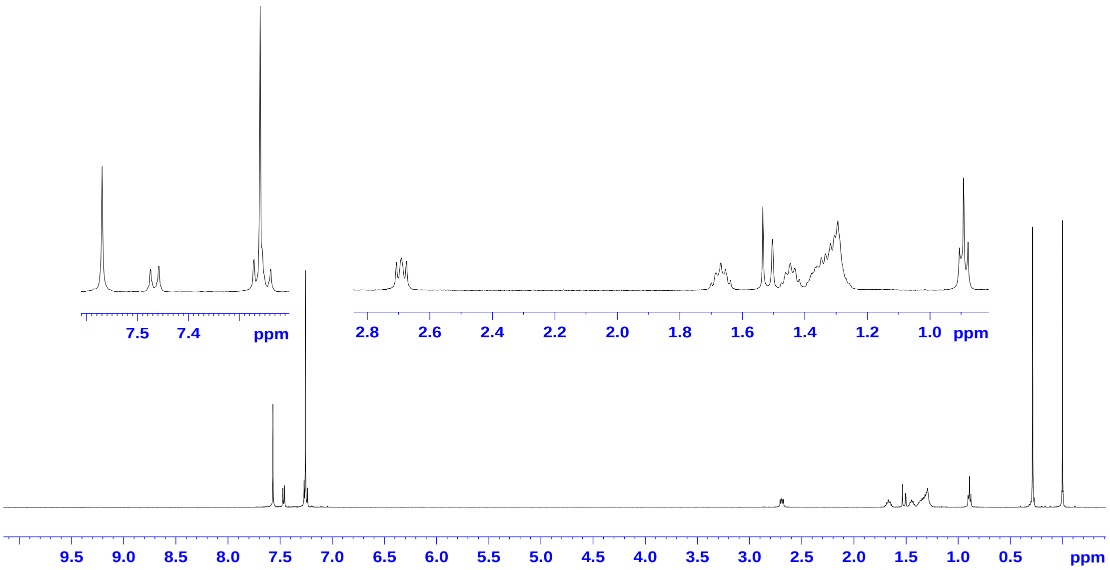
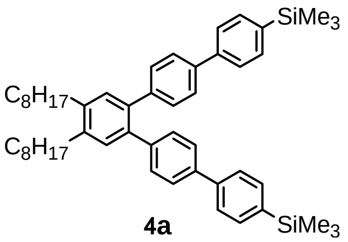


Figure S1a. ^{1}H NMR spectrum of **4a** in $CDCl_3$ at 25 °C.



4a

S11. ^{13}C NMR spectrum of 4a (125 MHz)

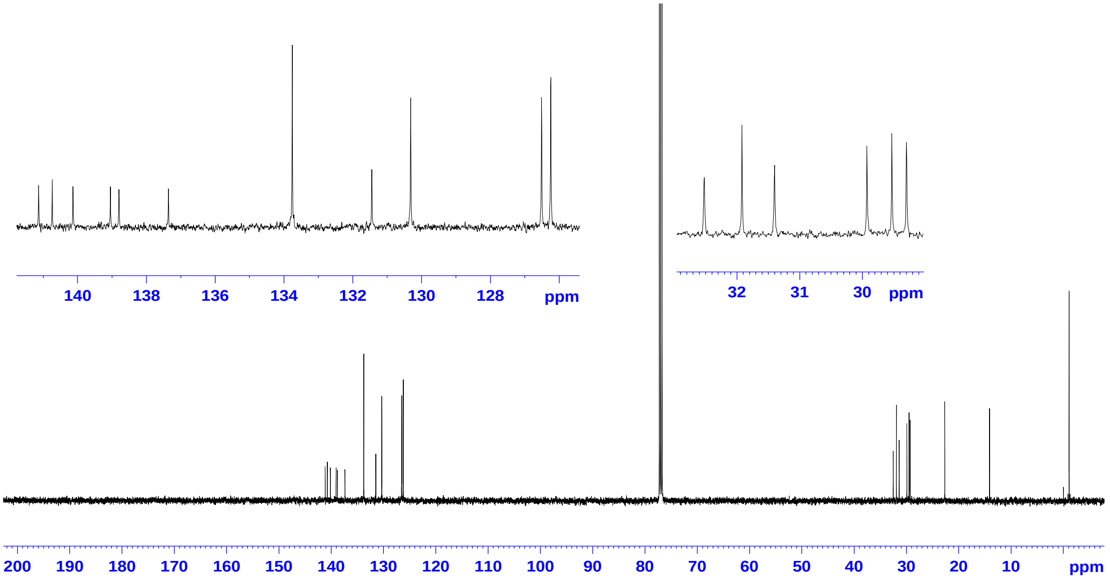


Figure S1b. ^{13}C NMR spectrum of **4a** in $CDCl_3$ at 25 °C.

S12. ^{1}H NMR spectrum of 4b (500 MHz)

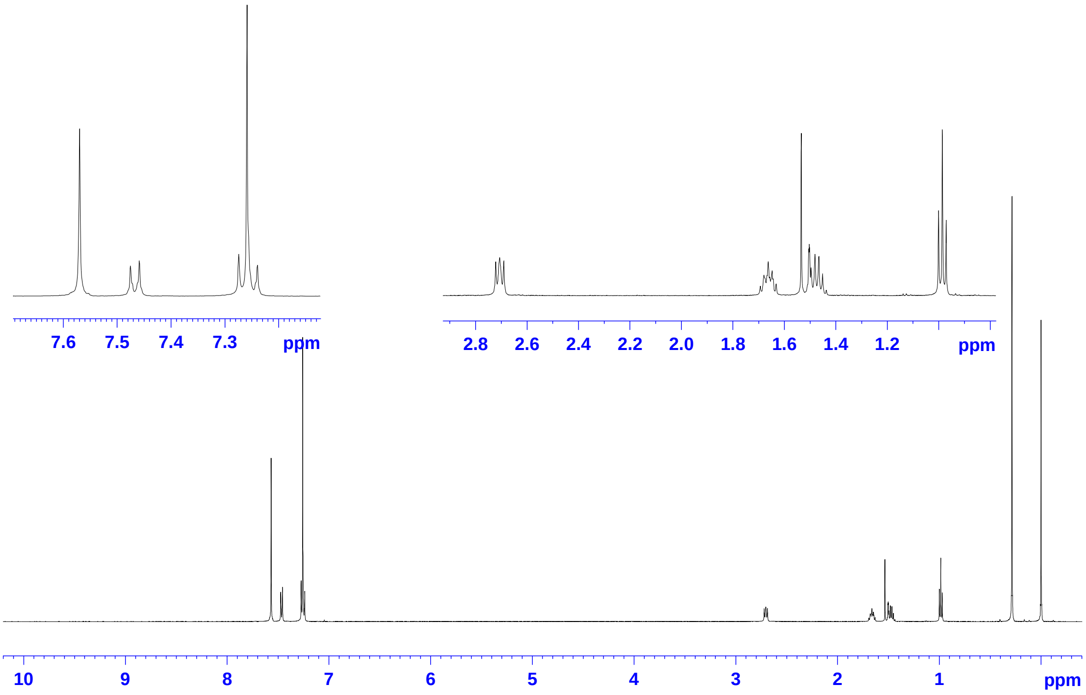


Figure S2a. ^{1}H NMR spectrum of **4b** in $CDCl_3$ at 25 °C.

S13. ^{13}C NMR spectrum of 4b (125 MHz)

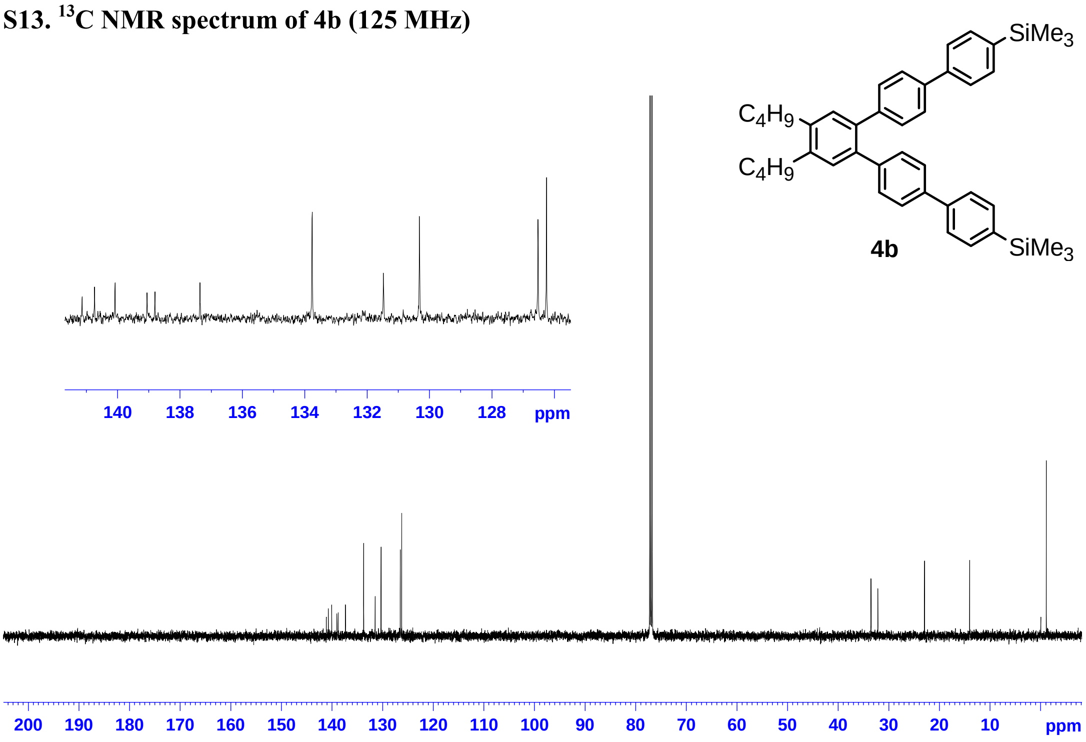


Figure S2b. ^{13}C NMR spectrum of **4b** in $CDCl_3$ at 25 °C.

S14. ^{1}H NMR spectrum of 5a (500 MHz)

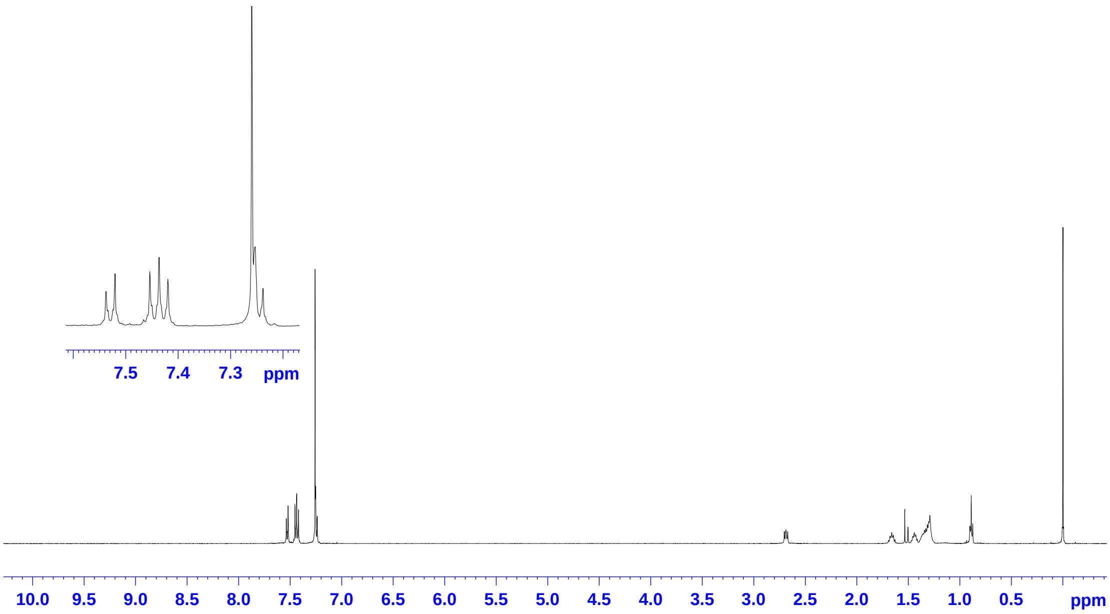
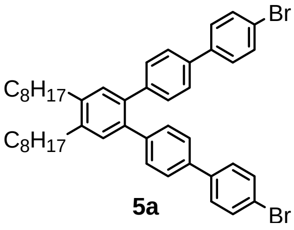


Figure S3a. ^{1}H NMR spectrum of **5a** in $CDCl_3$ at 25 °C.



5a

S15. ^{13}C NMR spectrum of 5a (125 MHz)

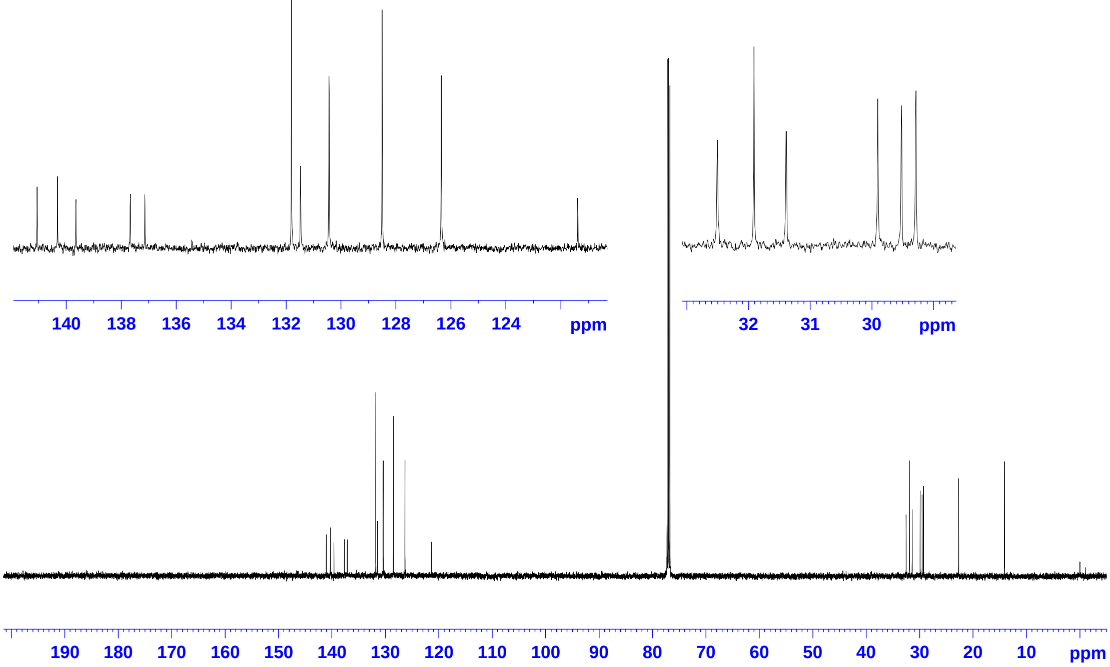


Figure S3b. ^{13}C NMR spectrum of **5a** in $CDCl_3$ at 25 °C.

S16. ^{1}H NMR spectrum of 5b (500 MHz)

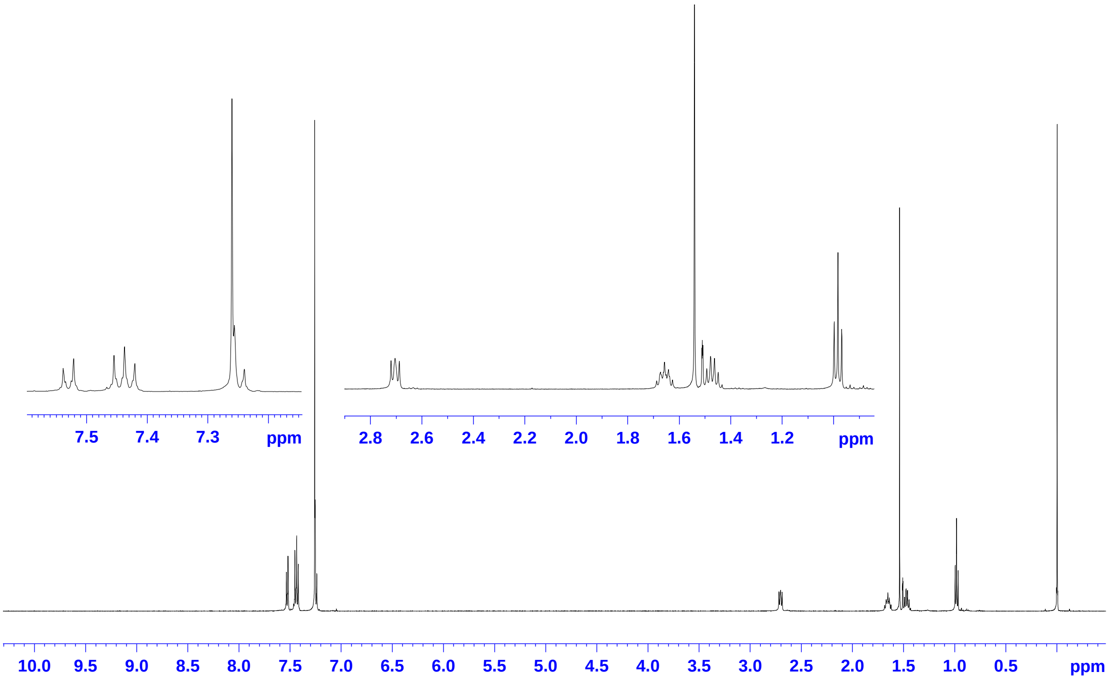
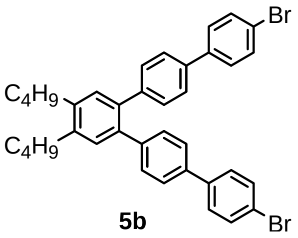


Figure S4a. ^{1}H NMR spectrum of **5b** in $CDCl_3$ at 25 °C.



5b

S17. ^{13}C NMR spectrum of 5b (125 MHz)

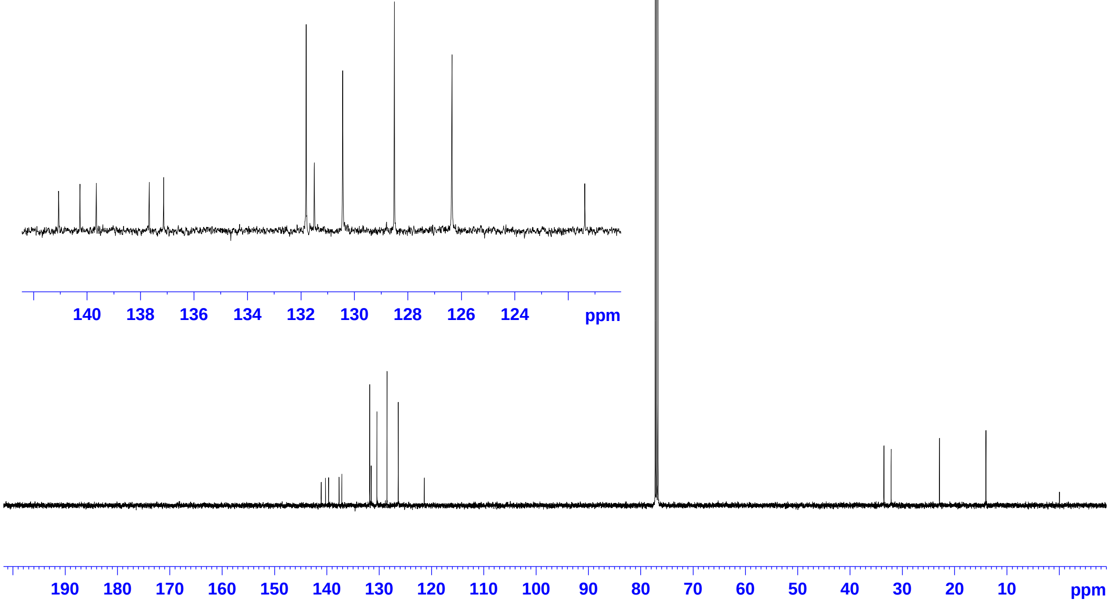


Figure S4b. ^{13}C NMR spectrum of **5b** in $CDCl_3$ at 25 °C.

S18. ^{1}H NMR spectrum of 5c (500 MHz)

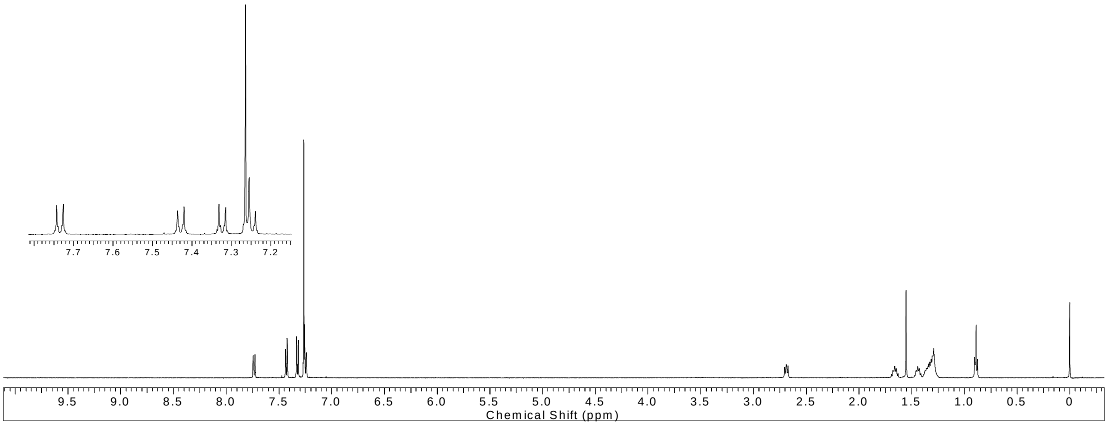
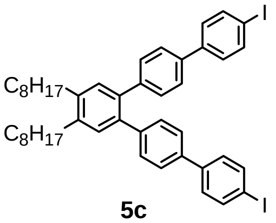


Figure S5a. ^{1}H NMR spectrum of **5c** in $CDCl_3$ at 25 °C.

S19. ^{13}C NMR spectrum of 5c (125 MHz)



5c

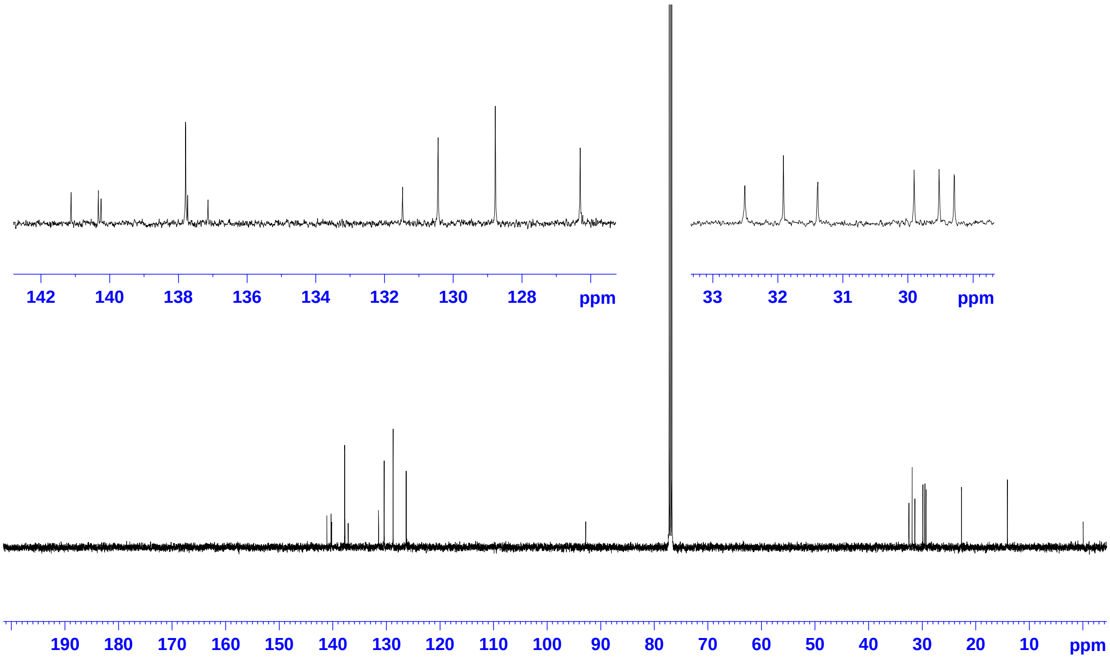


Figure S5b. ^{13}C NMR spectrum of **5c** in $CDCl_3$ at 25 °C.

S20. ^{1}H NMR spectrum of 1a (500 MHz)

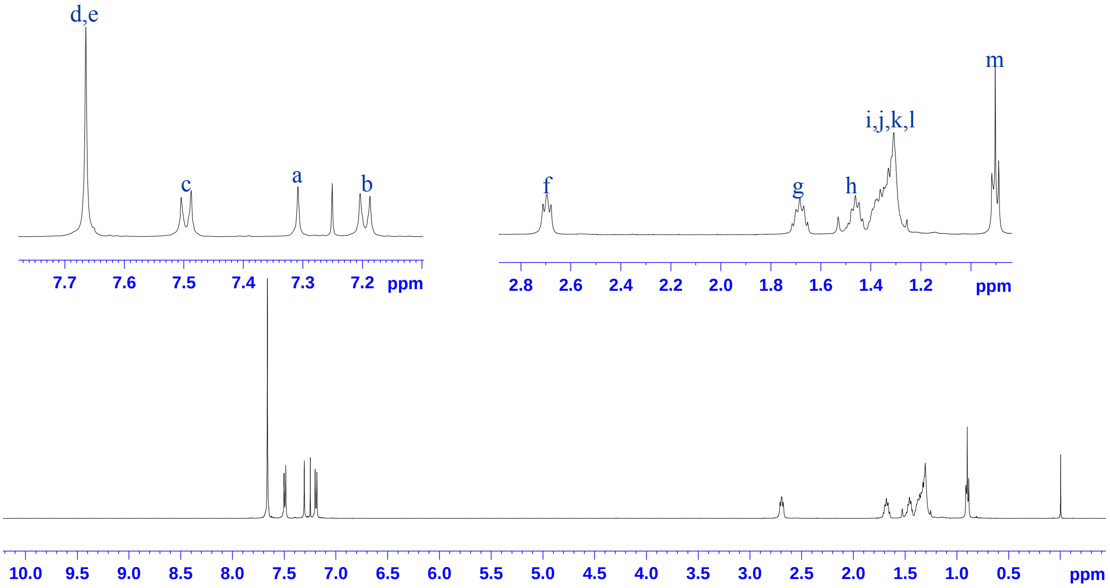


Figure S6a. ^{1}H NMR spectrum of **1a** in $CDCl_3$ at 25 °C.

S21. ^{13}C NMR spectrum of 1a (125 MHz)

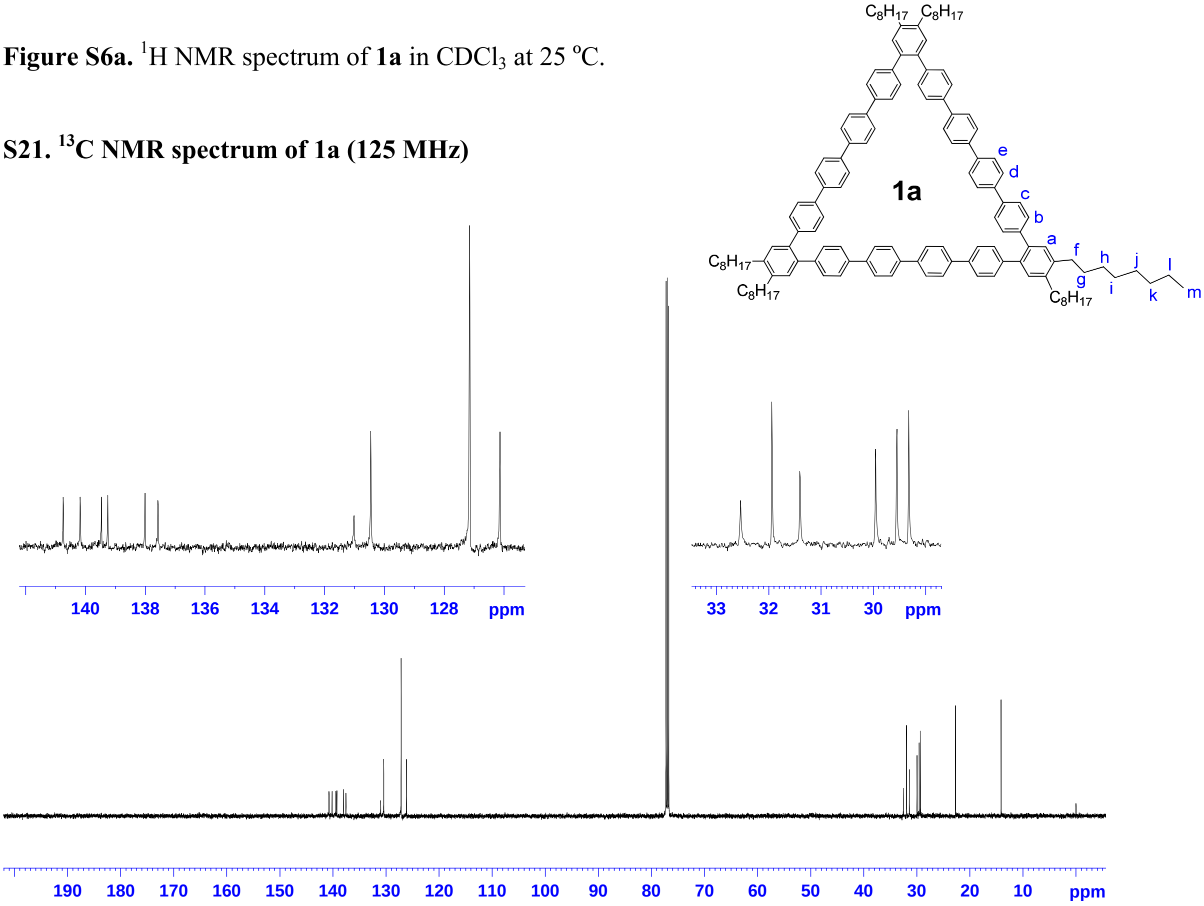


Figure S6b. ^{13}C NMR spectrum of **1a** in $CDCl_3$ at 25 °C.

S22. ^{1}H NMR spectrum of 1b (500 MHz)

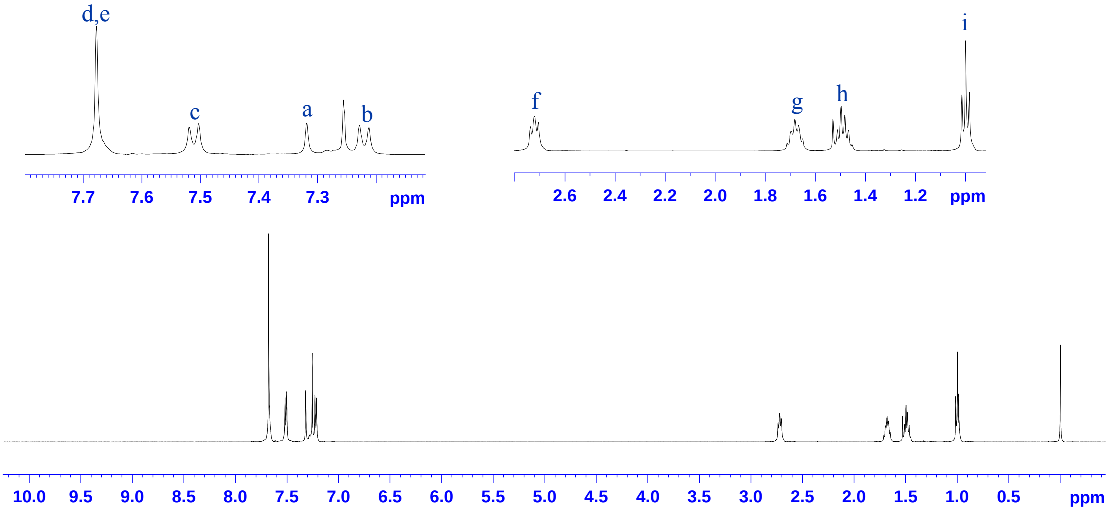
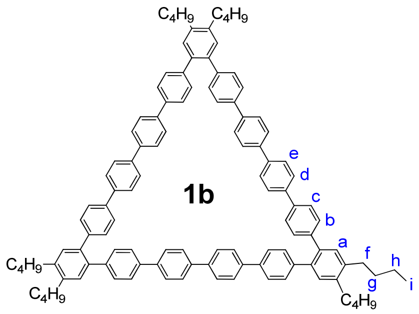


Figure S7a. ^{1}H NMR spectrum of **1b** in $CDCl_3$ at 25 °C.



S23. ^{13}C NMR spectrum of 1b (125 MHz)

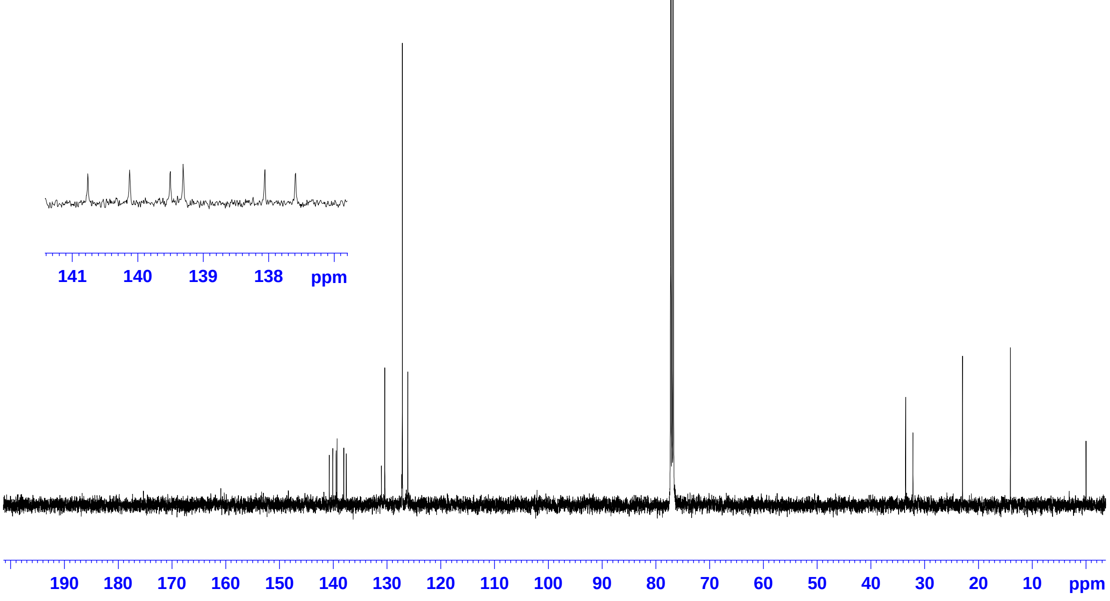


Figure S7b. ^{13}C NMR spectrum of **1b** in $CDCl_3$ at 25 °C.

S24. Absorption and emission spectra of 1a

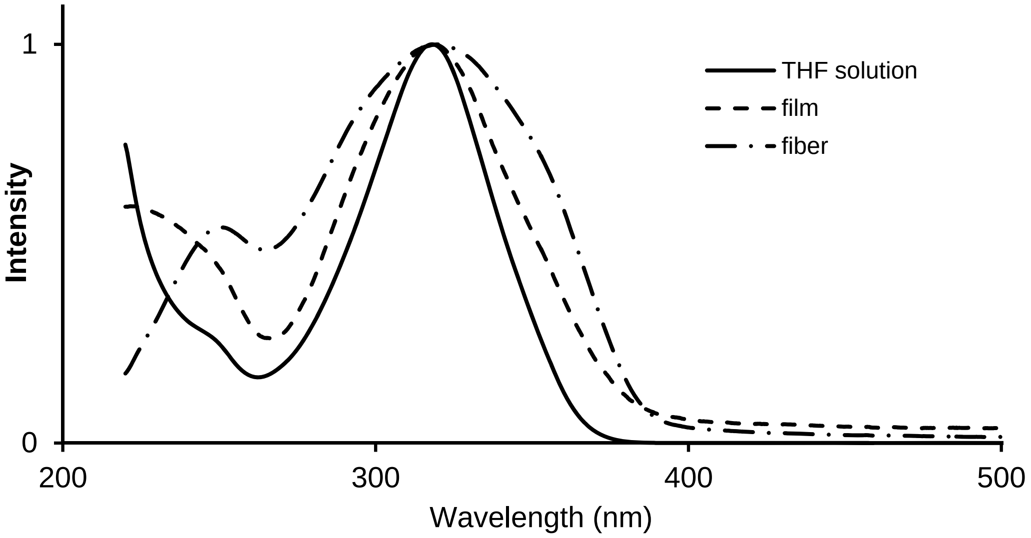


Figure S8a. UV-Vis spectra of **1a** (THF solution, drop cast film from THF, and fiber from benzene).

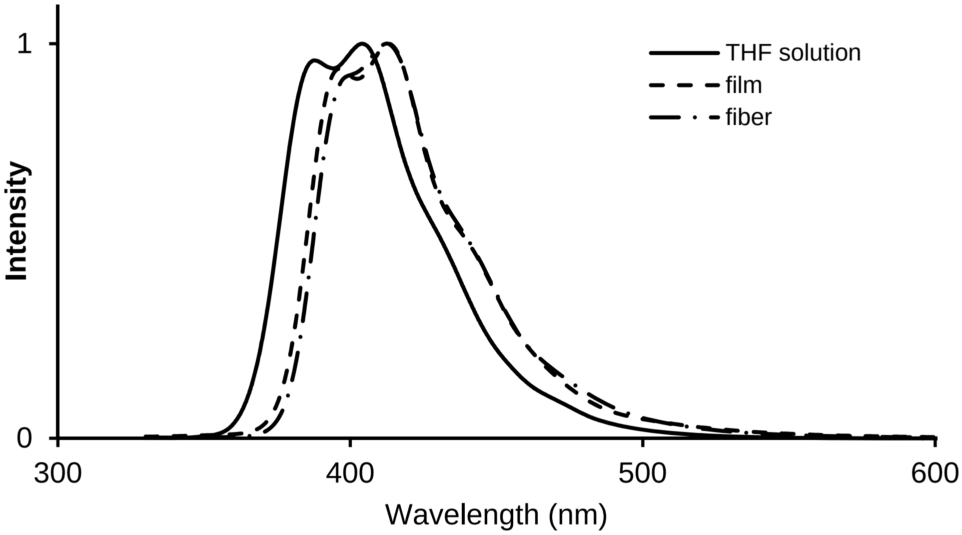


Figure S8b. Emission spectra of **1a** (THF solution, drop cast film from THF, and fiber from benzene).

S25. Absorption and emission spectra of 1b

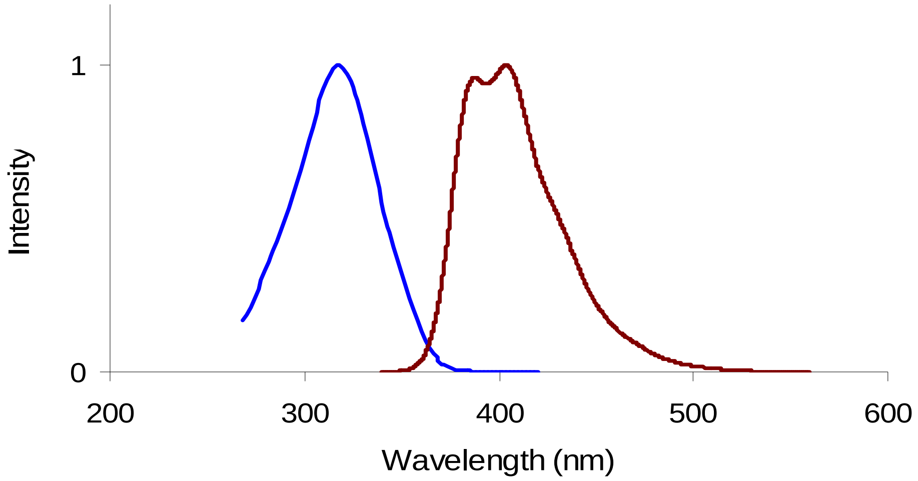
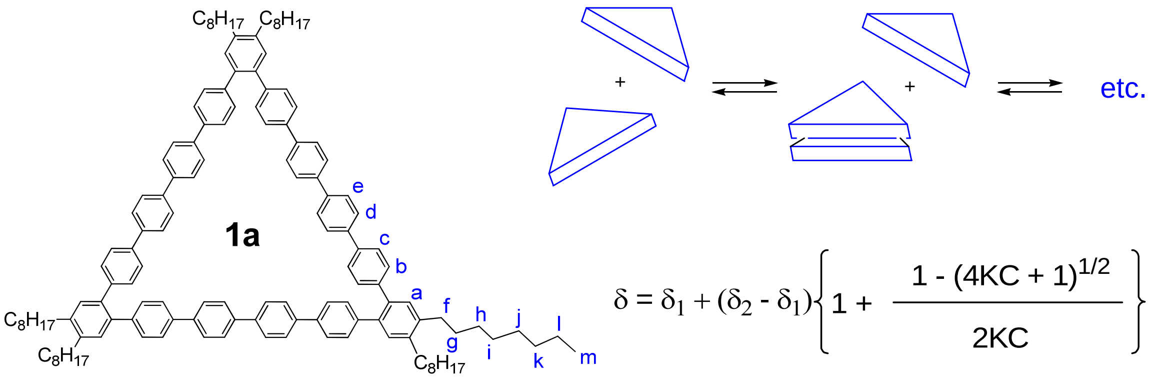


Figure S9. UV-Vis and fluorescence spectra of **1b** in THF.

S26. Self-aggregation behavior of 1a in solution

Pentadecaphenylene **1a** exhibited temperature dependent self-aggregation behavior in solution. ^{1}H NMR measurement at variable concentration in toluene-d_8 showed that the H$_b$ signal shifted downfield after gradual dilution. When the temperature was gradually lowered down to -20 °C the signals gradually shifted to upfield with broadening of signal. Treatment of concentration dependent ^{1}H NMR chemical shift of protons H$_b$ with least-square curve-fitting (isodesmic model) gives $\delta_1 = 7.552 \pm 0.013$ (ppm), $\delta_2 = 7.038 \pm 0.005$ (ppm) and $K = 5284 \pm 568$ (M^{-1}) in tolulene-d_8 at -20 °C, where the parameters δ_1 and δ_2 represent chemical shifts of monomer and oligomer respectively and K is the aggregation constant.



$$\delta = \delta_1 + (\delta_2 - \delta_1)\left\{1 + \frac{1 - (4KC + 1)^{1/2}}{2KC}\right\}$$

Figure S10. Self-aggregation of **1a** in solution

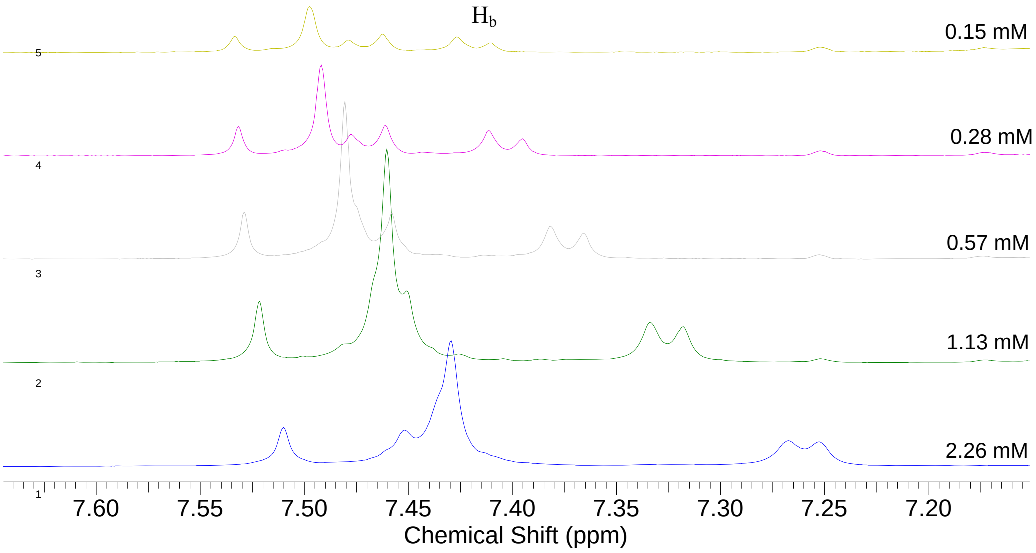


Figure S11a. Concentration-dependent ^{1}H NMR spectra of **1a** in toluene-d_8 at 293 K.

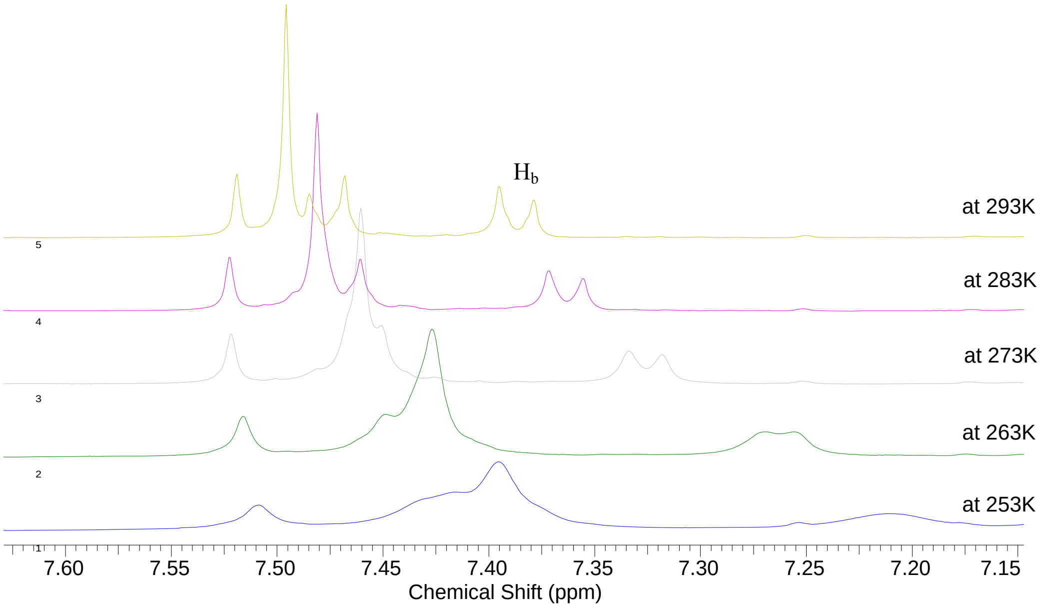


Figure S11b. Temperature-dependent ^{1}H NMR spectra of **1a** at concentration 1.13 mM in toluene-d_8.

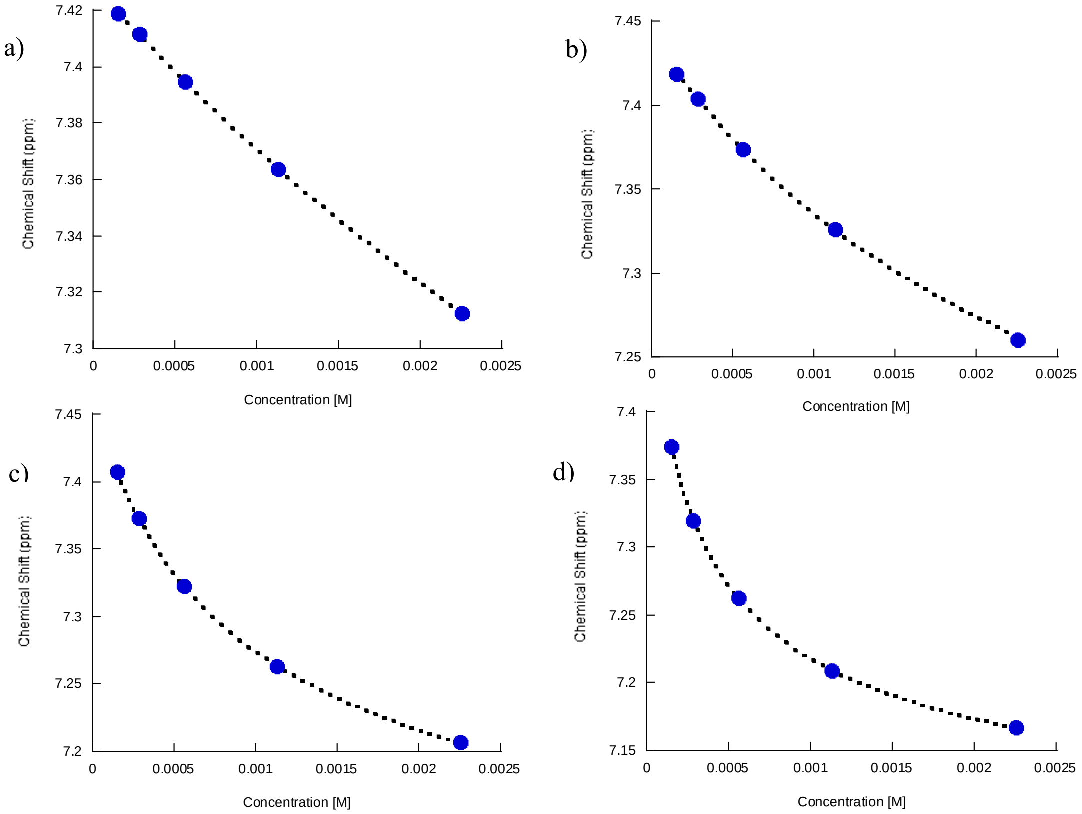


Figure S12. Plot of ^{1}H NMR chemical shift of H$_b$ versus concentration (a) at 283 K, (b) at 273 K, (c) at 263 K and (d) at 253 K.

Table S1. Chemical shift of protons H_b of **1a** in toluene-d_8 at variable concentrations and temperatures, calculated association constants, and calculated chemical shifts for monomer and oligomer.

Conc (mM)	253K	263K	273K	293K
2.26	7.1670	7.2067	7.2599	7.3126
1.13	7.2088	7.2631	7.3258	7.3636
0.57	7.2628	7.3223	7.3737	7.3948
0.28	7.3198	7.3725	7.4036	7.4115
0.15	7.3740	7.4074	7.4188	7.4188
δ_1	7.5524 ± 0.0130	7.4711 ± 0.0026	7.4426 ± 0.0031	7.4291 ± 0.0006
δ_2	7.0378 ± 0.0047	6.9772 ± 0.0064	6.8043 ± 0.0593	6.4099 ± 0.0975
K	5284 ± 568	1102 ± 56	244 ± 42	64 ± 8

S27. van't Hoff plot for self-aggregation of 1a in toluene-d_8

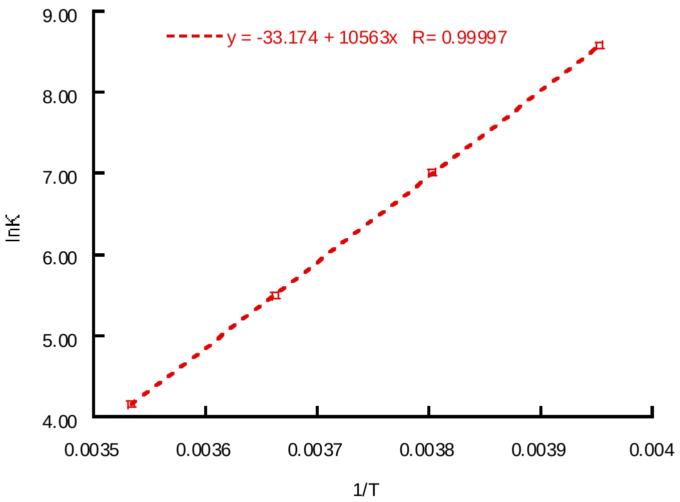


Figure S13. van't Hoff plot for self-aggregation of **1a** in toluene-d_8. Thermodynamic parameters for self-aggregation of **1a** in toluene-d_8 are $\Delta G = -5.57$ kJ mol^{-1} at 298 K, $\Delta H = -87.82$ kJ mol^{-1}, and $\Delta S = -276$ J K^{-1} mol^{-1}.

S28. Formation of fibers and films from 1a

Pentadecaphenylene **1a** formed nanofibers when a hot solution of **1a** in benzene (15 mg/ml) was allowed to stand at room temperature. The widths and lengths of nanofibers are 200–500 nm and more than 100 μm, respectively. The film of **1a** was prepared by drop-casting 1mM solution of **1a** in THF or in benzene on Al plate.

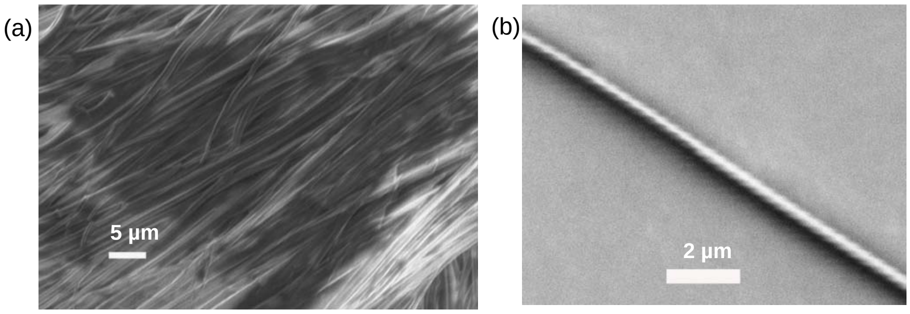


Figure S14a. SEM image of (a) **1a** fibers and (b) a portion of a single fiber.

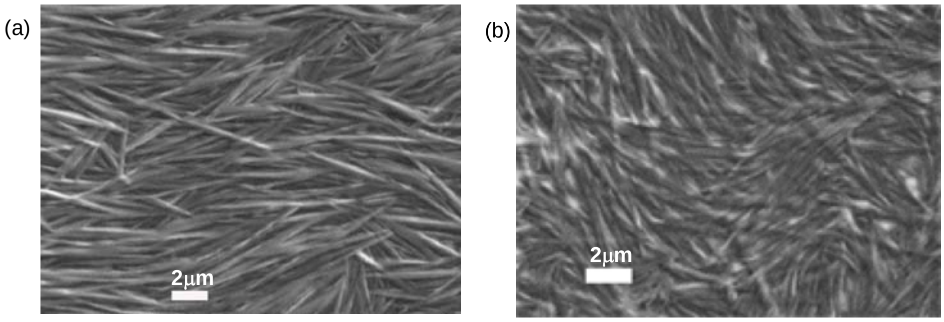


Figure S14b. SEM images of (a) **1a** film from THF and (b) **1a** film from benzene.

S29. Excitation spectra of film, fiber and THF solution of 1a

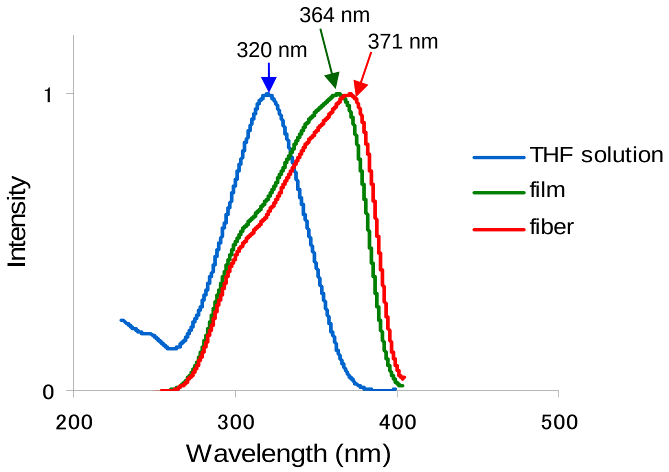


Figure S15. Excitation spectra of film (from THF), fiber (from benzene), and THF solution of **1a**.

S30. XRD profiles of 1a fiber and film

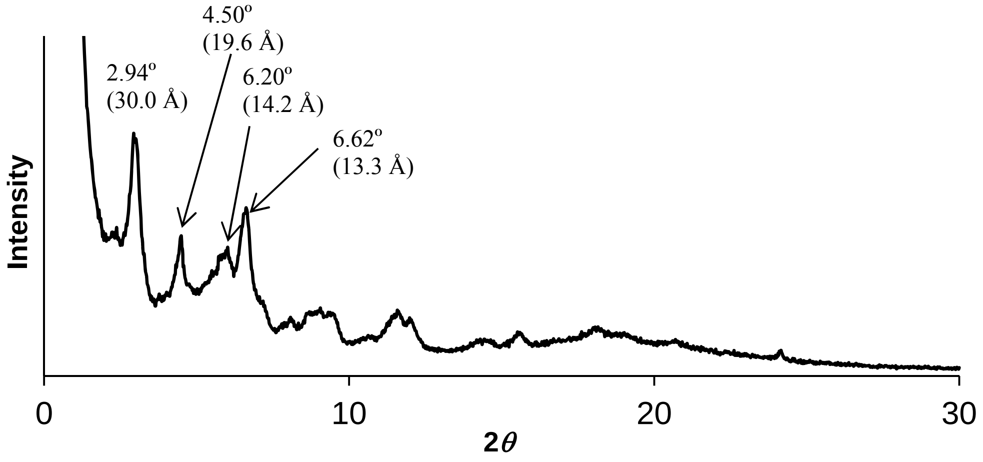


Figure S16a. XRD profile of **1a** fiber from benzene on Al plate.

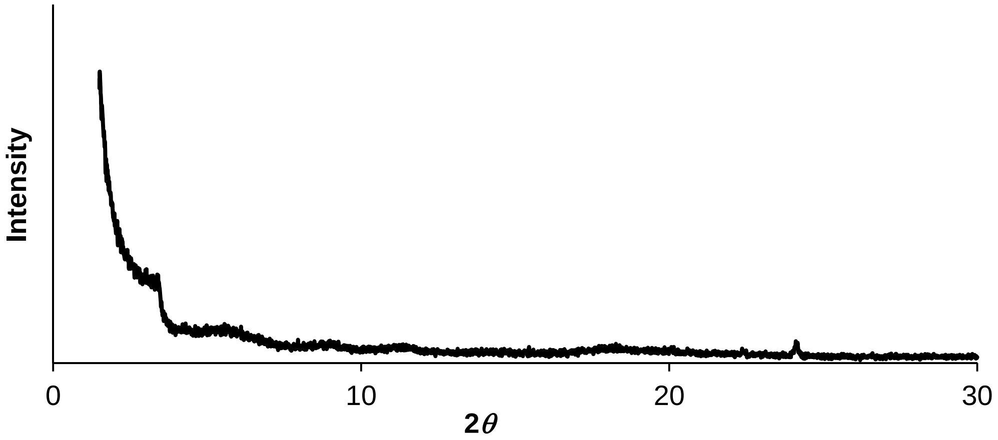


Figure S16b. XRD profile of **1a** film from benzene on Al plate.

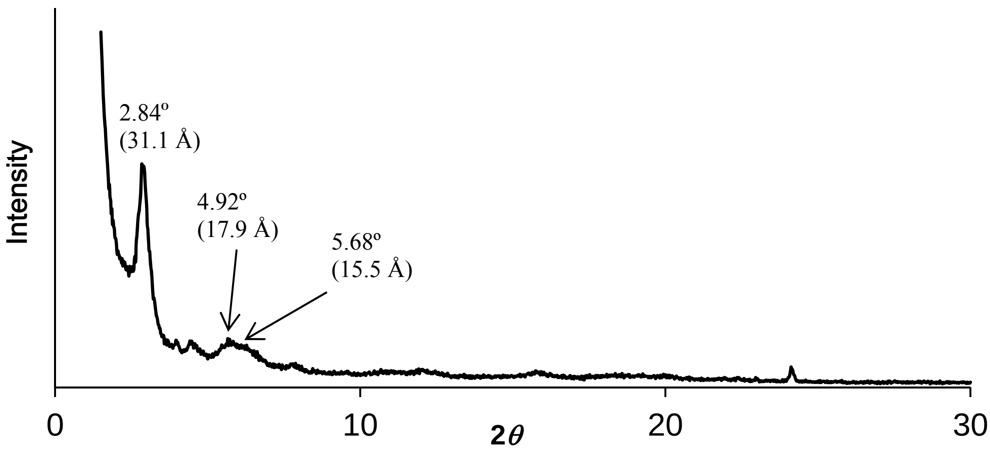


Figure S16c. XRD profile of **1a** film from THF on Al plate.

S31. Formation of fullerene complex in solution

Inclusion complex was formed when pentadecaphenylene **1a** was mixed with C_{60} in solution. The complex formation was investigated by UV-Vis spectroscopy. A Job plot monitored at 410 nm in toluene with a total concentration of 5.0×10^{-4} M showed a 1:1 **1a**·C_{60} complex formation. The fluorescence intensity of **1a** in toluene was quenched in the presence of C_{60}.

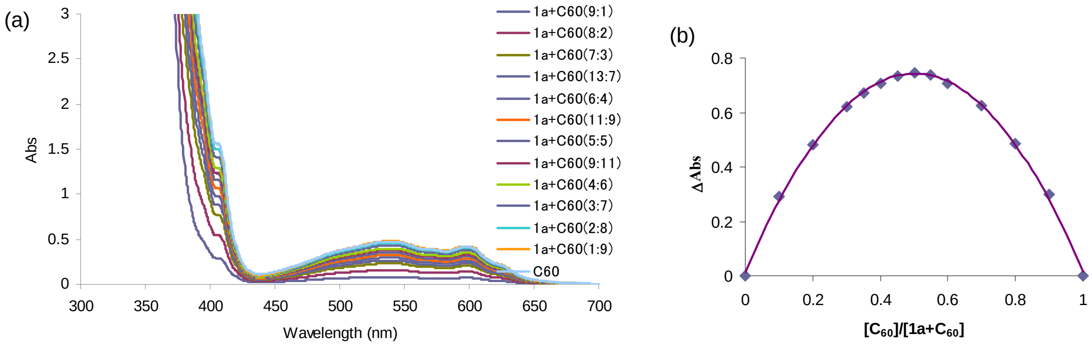


Figure S17. (a) UV-Vis spectra **1a**+C_{60} at various ratios in toluene and (b) Job plot of **1a** and C_{60}

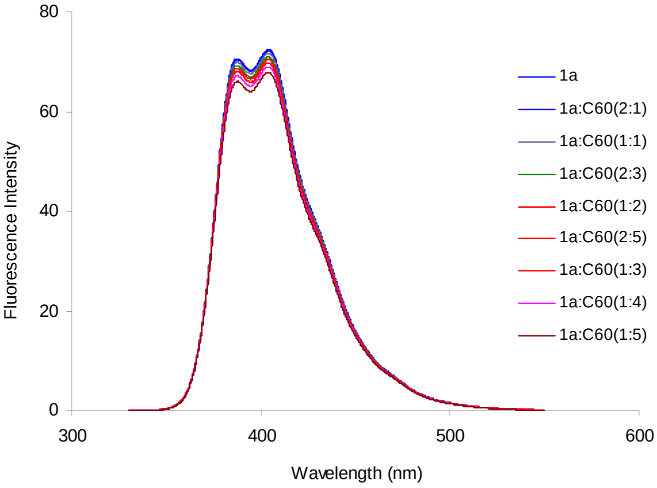
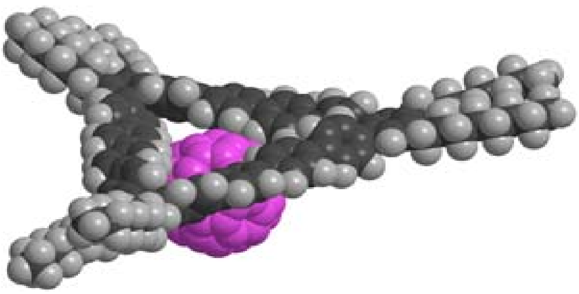


Figure S18. Quenching of fluorescence of **1a** in the presence of C_{60} in toluene.



A possible structure of the 1:1 **1a**·C_{60} complex

S32. ^{1}H NMR spectra of 1a and a mixture of 1a and C_{60} (1:1) in benzene-d_6 solution (500 MHz)

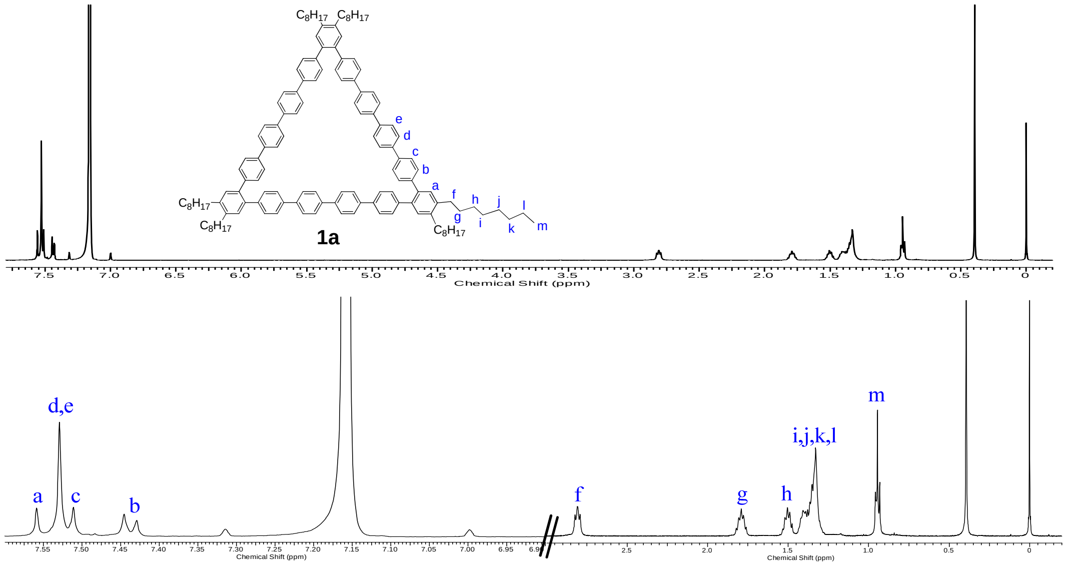


Figure S19a. ^{1}H NMR spectrum of **1a** solution (0.55 mM in benzene-d_6, 25°C).
^{1}H NMR (benzene-d_6, 500 MHz): δ (ppm) 7.559 (s, 6H, H_a), 7.529–7.511 (m, 36H, $H_{c\text{-}e}$), 7.437 (d, J = 8.2 Hz, 12H, H_b), 2.808 (t, J = 7.8 Hz, 12H), 1.822–1.760 (m, 12H), 1.533–1.475 (m, 12H), 1.422–1.330 (m, 48H), 0.945 (t, J = 6.8 Hz, 18H).

–

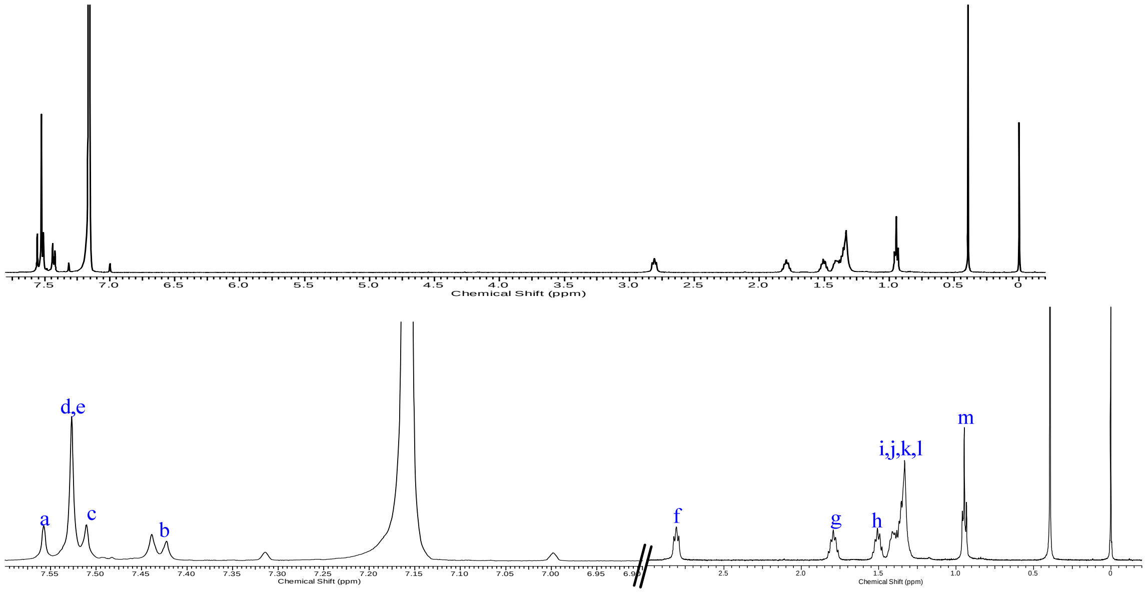


Figure S19b. ^{1}H NMR spectrum of the 1:1 **1a**–C_{60} solution (0.55 mM in benzene-d_6, 25°C).
^{1}H NMR (benzene-d_6, 500 MHz): δ (ppm) 7.558 (s, 6H, H_a), 7.527–7.510 (m, 36H, $H_{c\text{-}e}$), 7.431 (d, J = 8.2 Hz, 12H, H_b), 2.808 (t, J = 7.8 Hz, 12H), 1.824–1.763 (m, 12H), 1.537–1.480 (m, 12H), 1.425–1.333 (m, 48H), 0.946 (t, J = 6.8 Hz, 18H)

S33. Formation of gel from 1a.

[Formation of the **1a** gel]

Fibrous structure was formed from pentadecaphenylene **1a**. When a hot solution of **1a** (15 mg, 8.2×10^{-6} mol) in benzene (1 ml) was allowed to stand at room temperature, a white gel was formed. The SEM image of the xerogel showed fiber formation with widths 200−500 nm and lengths more than 100 μm. Hexane was added to the gel, and fibrous material was separated out by filtration. As compared with the ^{1}H NMR data of **1a** in solution (0.55 mM), aromatic protons showed the upfield shift by ~ 0.06 ppm and octyl protons except for the benzylic position exhibited the downfield shift by ~ 0.01 ppm indicate the self-aggregation of **1a**.

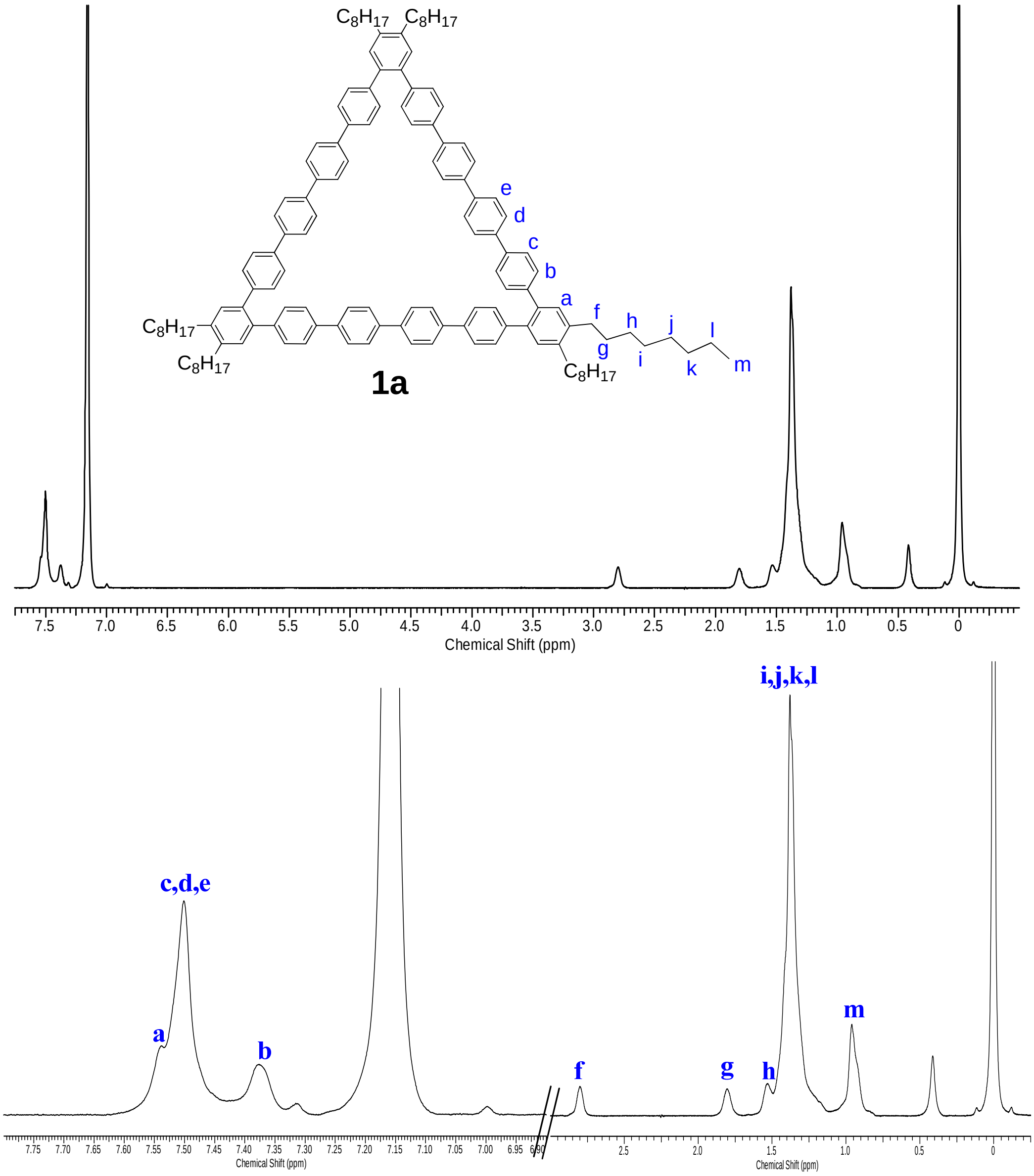


Figure S20. ^{1}H NMR spectrum of the **1a** gel (8.27 mM in benzene-d_6) at 25°C.

^{1}H NMR (benzene-d_6, 500 MHz): δ (ppm) 7.538 (broad s, 6H, H_a), 7.501 (broad m, 36H, $H_{c\text{-}e}$), 7.373 (broad d, 12H, H_b), 2.799 (broad t, 12H), 1.804 (broad m, 12H, H_f), 1.534 (broad m, 12H, H_g), 1.379 (broad m, 48H, $H_{h\text{-}l}$), 0.959 (broad t, 18H, H_m).

S34. Fluorescence lifetime measurements of 1a and 1:1 1a–C_{60} solution

The fluorescence spectra and lifetimes were measured by a photon counting method with a streak scope (Hamamatsu Photonics, C4334-01) using the second harmonic generation (SHG, 370 nm) of a Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, fwhm = 150 fs) as an excitation source. Fluorescence decay profile was estimated from the streak image in 400−500 nm region. Estimation of the fluorescence lifetime has been done by the software equipped with the instrument. Fluorescence lifetime measurements were carried out at 293 K.

The fluorescence decays of **1a** (0.15 mM) fitted with a single exponential function satisfactory and its lifetimes were estimated as 860 ps. On the other hand, **1a** (0.15 mM) with C_{60} (0.15 mM) were fitted with a double exponential function satisfactory and the fast and slow lifetimes and their fractions were evaluated as 530 ps (20%) and 860 ps (80%), respectively. Note that slow component is the same as one of **1a**. Thus, the fast component may be the lifetime of **1a**-C_{60} complex. The fraction of the fast and slow components was the molar fraction in the complex formation in the ground state, therefore, we could estimate the association constant between **1a** and C_{60} in toluene as $K_a = 2.1\times10^3$ M $^{-1}$.

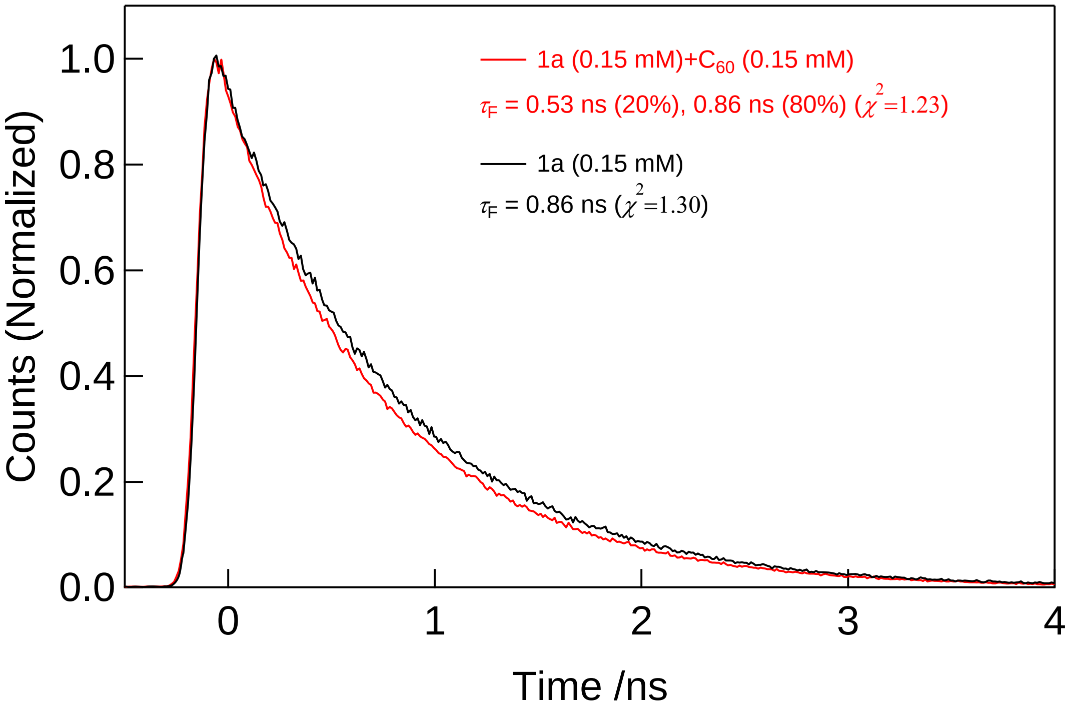


Figure S21. Fluorescence decay profile of **1a**–C_{60} (red) and **1a** (black) in toluene. Lifetimes and their fraction of **1a** with and without C_{60} were shown in the figure.

S35. Formation of gels from 1a and C_{60}

By mixing **1a** with 0.5, 0.75, 1.0, and 1.5 molar equiv. of C_{60} in hot benzene, dark brown gels composed of 2:1, 1.5:1, 1:1, and 1:1.5 **1a**·C_{60} gel formed, and almost all C_{60} was incorporated in the gels. Thus, a mixture of **1a** and C_{60} in a ratio of 6.9 mg and 1.4 mg (2:1), 5.5 mg and 1.5 mg (1.5:1), 4 mg and 1.6 mg (1:1), and 3.2 mg and 1.9 mg (1:1.5) forms gels. It is noteworthy that an increase in amounts of C_{60} enhances the gelation ability.

[Formation of the 1:1 **1a**·C_{60} gel and isolation of the 2:1 **1a**·C_{60} complex]

Fibrous structure was formed from pentadecaphenylene **1a** and C_{60} (1:1). When a hot solution of a mixture of **1a** (8.0 mg, 4.4×10^{-6} mol) and C_{60} (3.2 mg, 4.4×10^{-6} mol, 1 molar equiv.) in benzene (2 ml) was allowed to stand at room temperature, a dark drown gel was formed, which contained almost no free C_{60}. The SEM image of the xerogel showed fiber formation with widths 100−400 nm and lengths more than 100 μm. Hexane was added to the gel, and the fibrous material was separated by filtration. The purple filtrate contained uncomplexed C_{60}. After drying the brownish black solid (Y: 81%) under vacuum, it was subjected to elemental analysis. The result of elemental analysis is as follows: C, 92.50% and H, 7.50% which corresponds to the 2:1 complex of **1a** and C_{60} (calcd C, 92.77%; H, 7.23%).

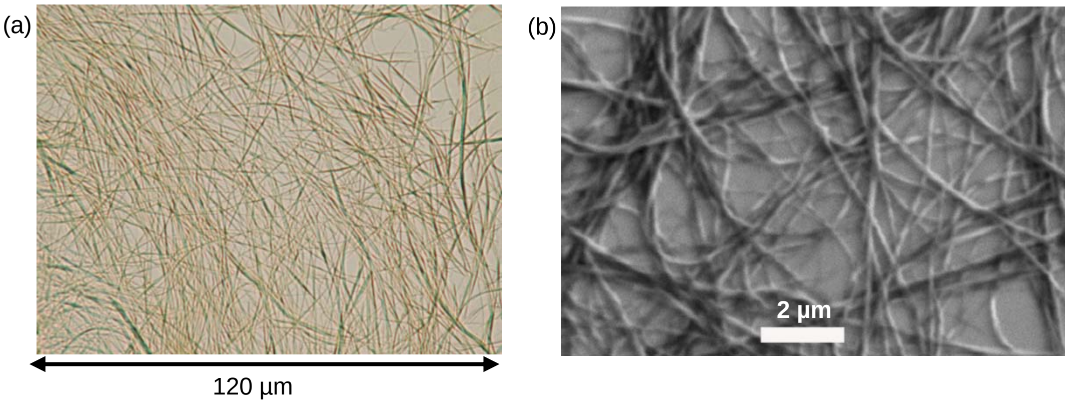
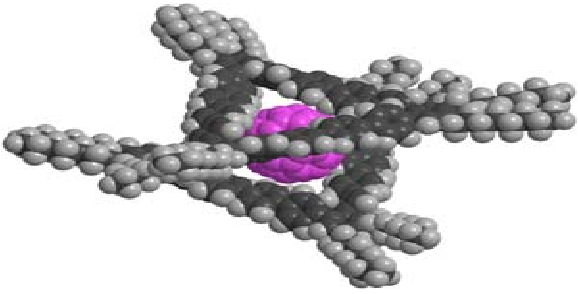


Figure S22. (a) Optical micrograph and (b) SEM image of the 2:1 **1a**·C_{60} fiber.



A possible structure of the 2:1 **1a**·C_{60} complex

[Formation of the 2:1 **1a**·C_{60} gel]

Fibrous structure was formed from pentadecaphenylene **1a** and C_{60} (2:1). When a hot solution of a mixture of **1a** (5.5 mg, 3.0×10^{-6} mol) and C_{60} (1.1 mg, 1.5×10^{-6} mol, 0.5 molar equiv.) in benzene (0.8 ml) was allowed to stand at room temperature, a dark brown gel was formed. The SEM image of the xerogel showed fiber formation with widths 100−400 nm and lengths more than 100 μm. Hexane was added to the gel, and fibrous material was separated out by filtration. After drying the brownish black material under vacuum, the 2:1 **1a**·C_{60} fiber was obtained in 86% yield.

S36. ^{1}H NMR spectra of the gels of 1a, 1a·C$_{60}$ (2:1), and 1a·C$_{60}$ (1:1) in benzene-d_6 (500 MHz)

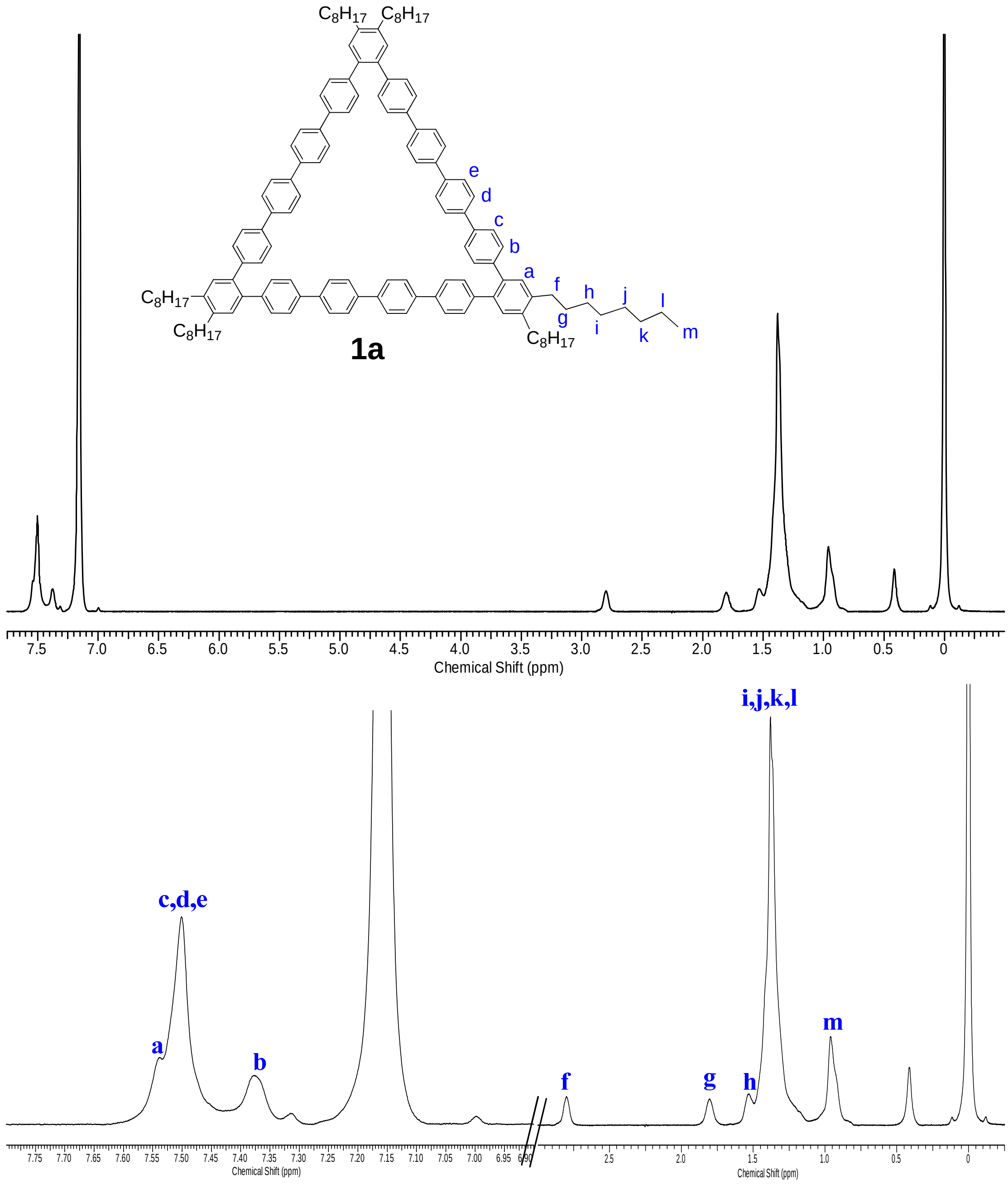


Figure S23a. ^{1}H NMR spectrum of the **1a** gel (8.27 mM in benzene-d_6) at 25°C.

^{1}H NMR (benzene-d_6, 500 MHz): δ (ppm) 7.54 (broad s, 6H, H$_a$), 7.50 (broad m, 36H, H$_{c\text{-}e}$), 7.37 (broad d, 12H, H$_b$), 2.80 (broad t, 12H), 1.81 (broad m, 12H, H$_f$), 1.53 (broad m, 12H, H$_g$), 1.38 (broad m, 48H, H$_{h\text{-}l}$), 0.96 (broad t, 18H, H$_m$).

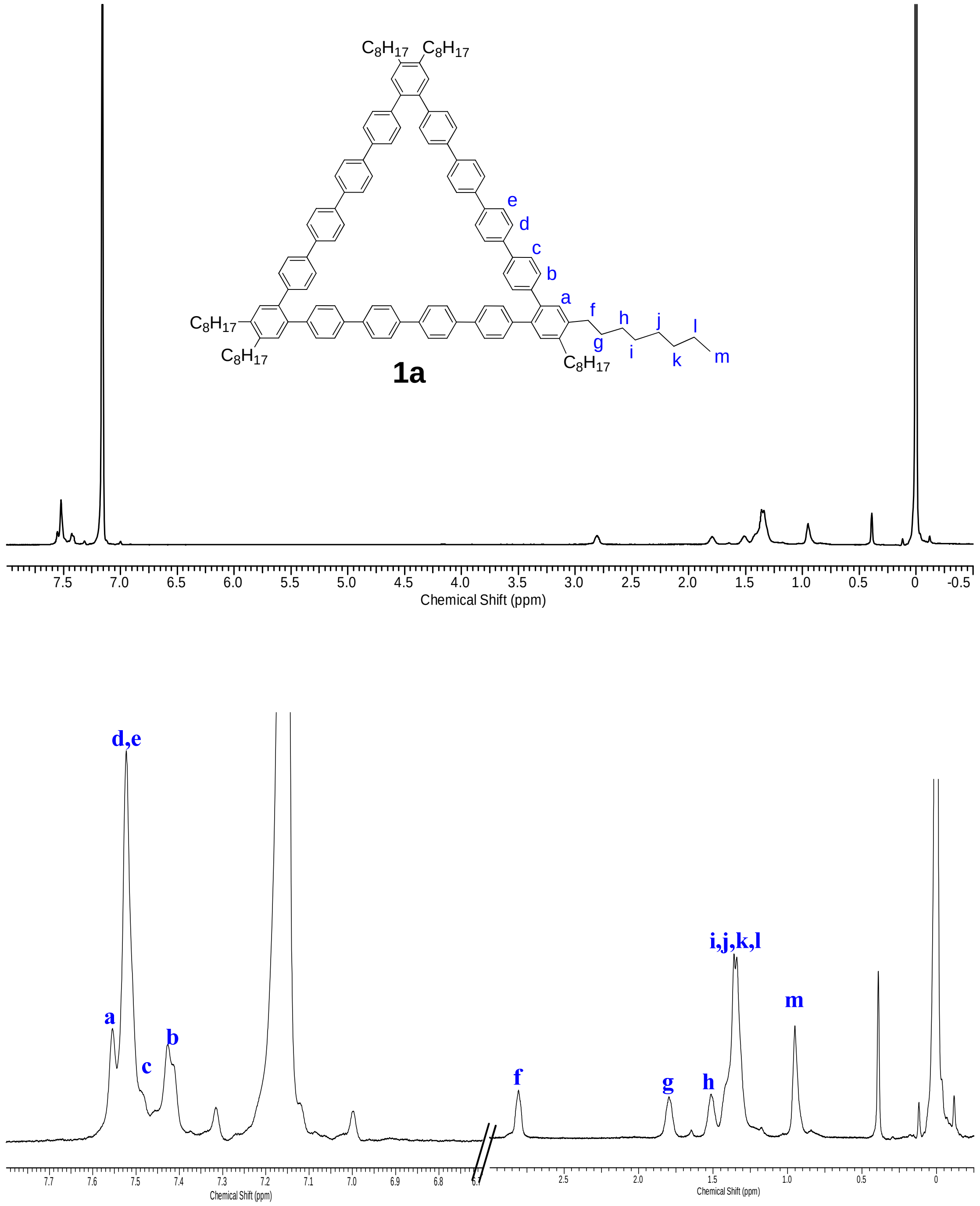


Figure S23b. ^{1}H NMR spectrum of the 2:1 **1a**·C_{60} gel (3.79 mM in benzene-d_6) at 25°C.

^{1}H NMR (benzene-d_6, 500 MHz): δ (ppm) 7.55 (s, 6H), 7.52−7.48 (broad m, 36H), 7.42 (d, J = 6.9 Hz, 12H), 2.81 (broad t, 12H), 1.80 (broad m, 12H), 1.52 (broad m, 12H), 1.41−1.36 (m, 48H), 0.95 (broad t, 18H).

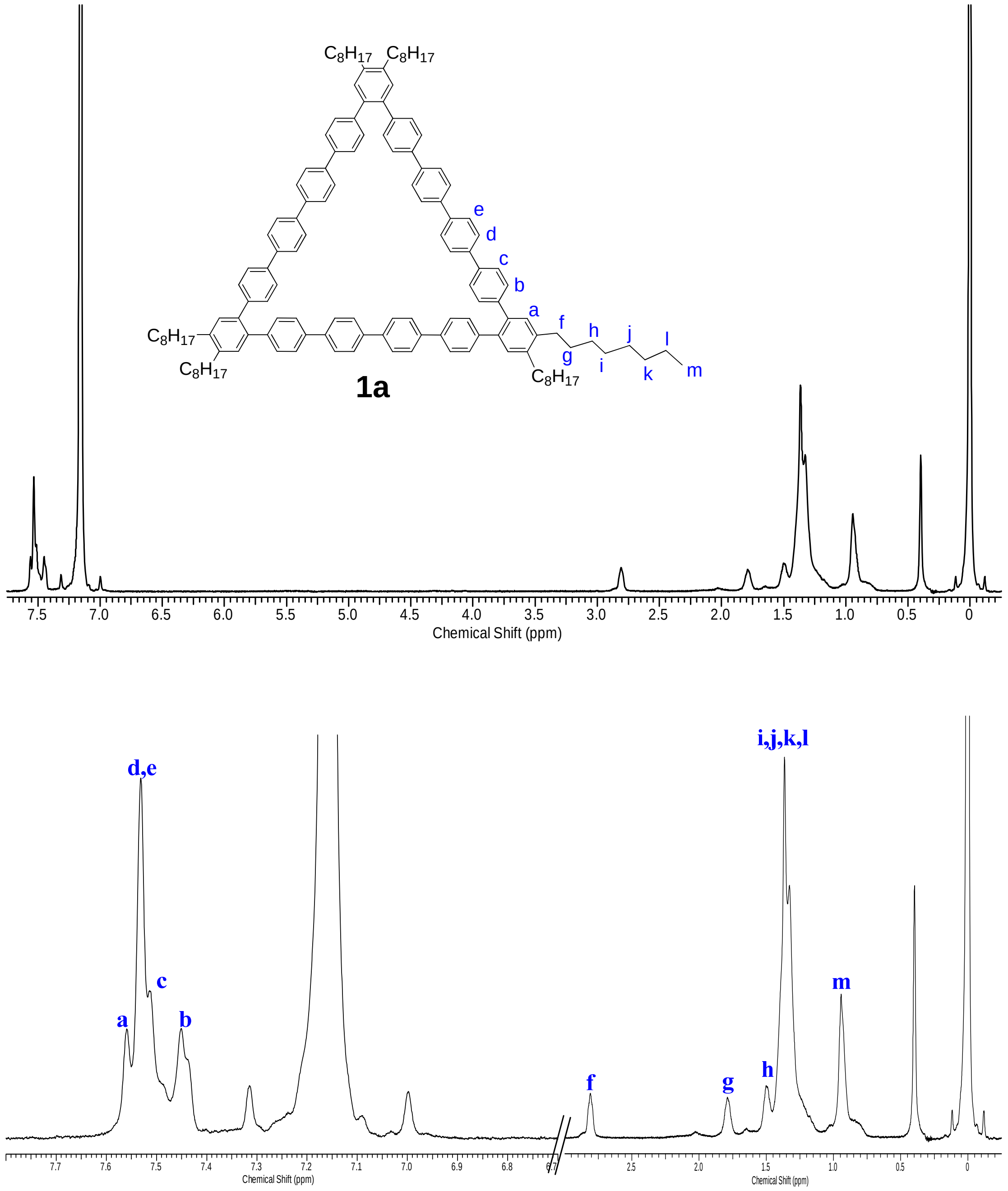


Figure S23c. ^{1}H NMR spectrum of the 1:1 **1a**·C_{60} gel (3.79 mM in benzene-*d*$_6$) at 25°C.

^{1}H NMR (benzene-*d*$_6$, 500 MHz): δ (ppm) 7.56 (s, 6H), 7.53−7.49 (broad m, 36H), 7.45 (d, *J* = 6.3 Hz, 12H), 2.81(broad t, 12H), 1.79 (broad m, 12H), 1.49 (broad m, 12H), 1.40-1.33 (m, 48H), 0.94 (broad t, 18H).

S37. XRD profiles of the rexogels of 1a·C_{60} (2:1) and 1a·C_{60} (1:1)

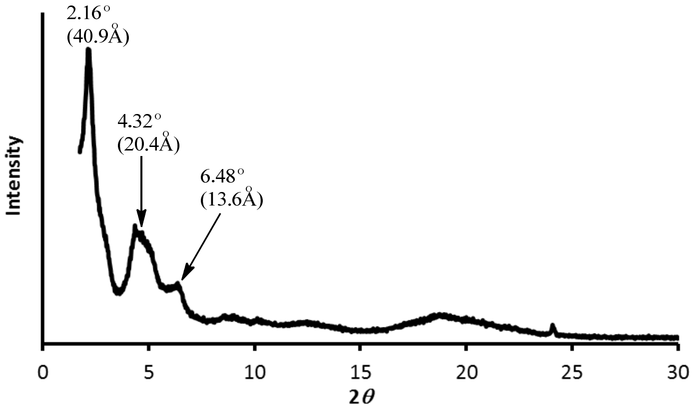


Figure S24a. XRD profile of the 2:1 **1a**·C_{60} xerogel (fiber) from benzene.

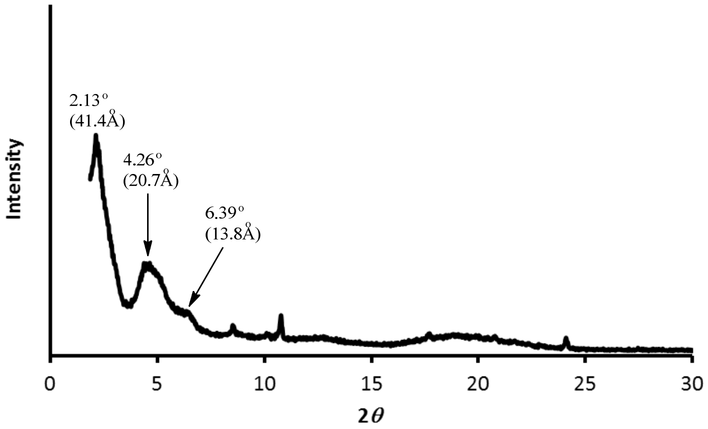


Figure S24b. XRD profile of the 1:1 **1a**·C_{60} xerogel (fiber) from benzene.

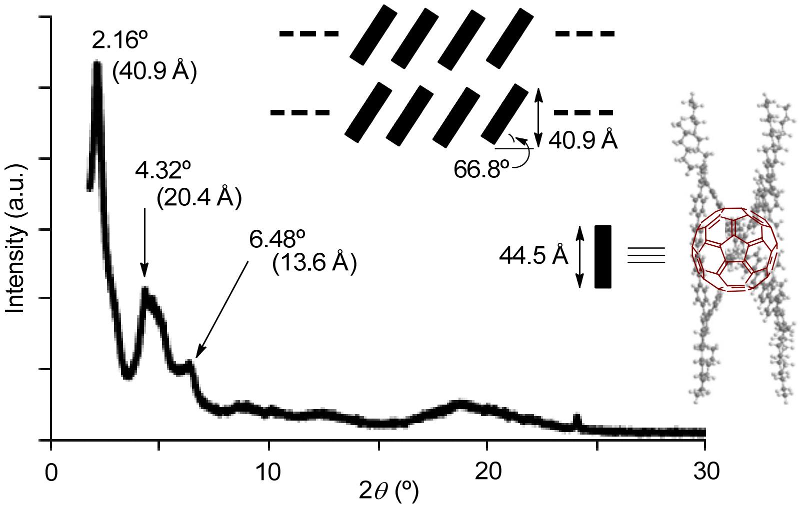


Figure S24c. XRD profile of the fiber of the 2:1 **1a**·C_{60} sandwich complex from benzene. The 2:1 **1a**·C_{60} fiber mainly have a lamellar form, and a giant **1a**–C_{60}–**1a** sandwich complex is aligned lamellarly and stacked in the direction of the fiber.

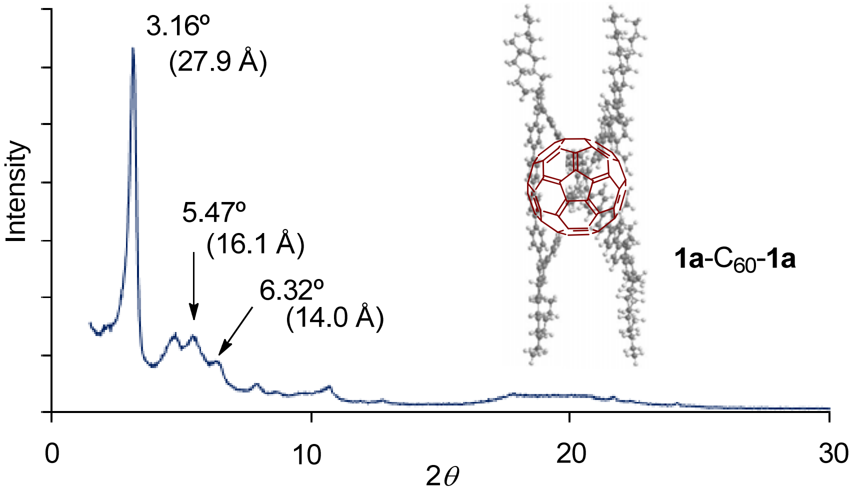


Figure S24d. XRD profile of the fiber of the 2:1 **1a**·C_{60} sandwich complex from hexane–benzene.

S38. Partial 2:1, 1.5:1, and 1:1 1a·C_{60} gels.

Partial gels were prepared from mixtures of **1a** and C_{60} in a molar ratio of 2:1, 1.5:1, and 1:1 in benzene. Thus, a mixture of **1a** and C_{60} in a ratio of 2:1 (4.1 mg and 0.8 mg), 1.5:1 (3.9 mg and 1.0 mg), or 1:1 (3.9 mg and 1.6 mg) formed a partial gel. In each case, excess C_{60} molecules were intercalated between the **1a**–C_{60}–**1a** sandwich complex to form gel, and each solution part composed of a small amount of **1a** and C_{60} showed a similar UV-vis spectrum.

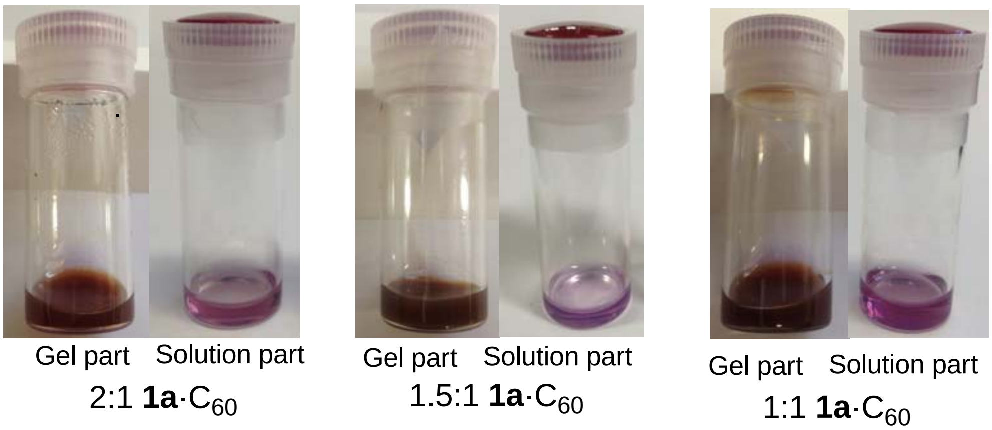


Figure S25. Photographs of the gel parts and solution parts separated from partial 2:1, 1.5:1, and 1:1 **1a**·C_{60} gels.

These experiments showed that a dark brown gel formed from a mixture of **1a** and 0.5 equiv. of C_{60} in benzene. When excess amounts of C_{60} were added, C_{60} molecules were intercalated between the **1a**–C_{60}–**1a** sandwich complex, and therefore, 2:1, 1.5:1, and 1:1 **1a**·C_{60} gels showed similar XRD profiles. The ^{13}C NMR measurements of 2:1, 1.5:1, and 1:1 **1a**·C_{60} gels and C_{60} in benzene solution only exhibited a singlet at the same position (δ = 143.62 at 25 °C).

S39. Molecular orbitals calculations of 1c at B3LYP/6-31G(d) level

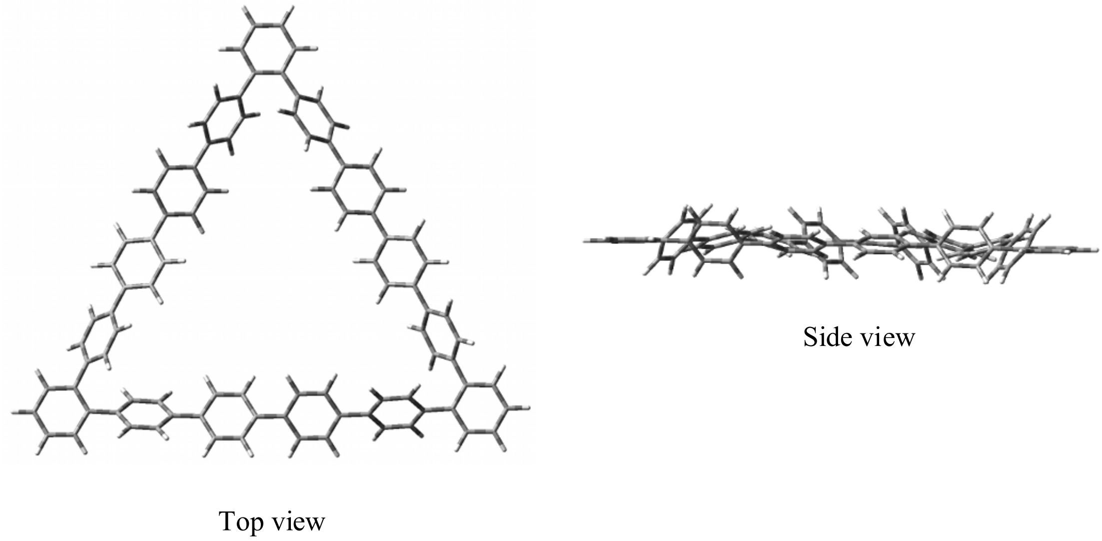


Figure S24. Optimized structure of **1c.**

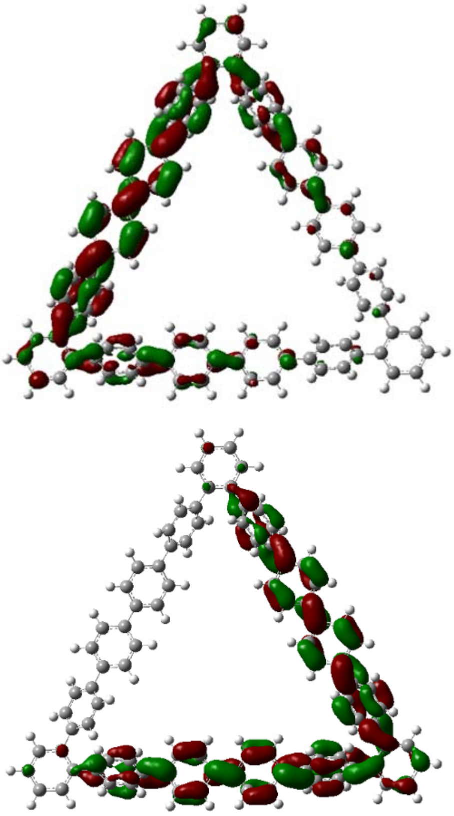
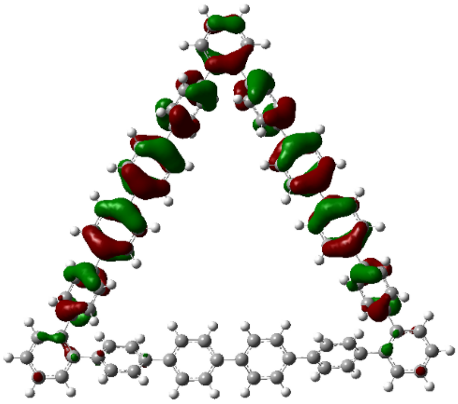


Figure S25a. LUMO of **1c**.

HOMO
(-5.4410 eV)



HOMO – 1
(-5.4410 eV)

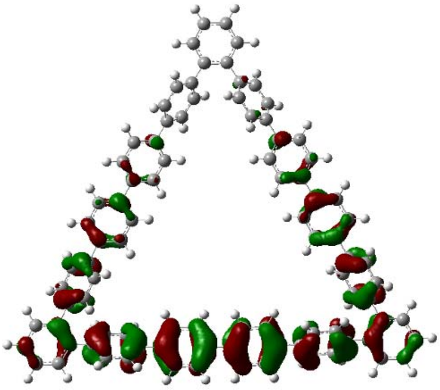


Figure S25b. HOMO of **1c**.

S40. Optimized structure of 1c (C_3 Symmetry)

Table S2. Cartesian coordinate of optimized geometry of **1c** at the B3LYP/6-31G(d) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.414476	11.197236	-0.047943
2	6	0	2.162255	12.384675	-0.101388
3	6	0	1.551979	13.636394	-0.082941
4	1	0	3.246317	12.314478	-0.124040
5	1	0	2.159108	14.536942	-0.117261
6	6	0	2.149695	9.901399	-0.008277
7	6	0	1.907966	8.951261	0.996784
8	6	0	2.606295	7.750238	1.031784
9	6	0	3.574169	7.438571	0.060746
10	6	0	3.832973	8.400110	-0.929459
11	6	0	3.138978	9.607569	-0.959637
12	1	0	1.168431	9.161484	1.763086
13	1	0	2.412442	7.048980	1.838353
14	1	0	4.556661	8.184102	-1.710465
15	1	0	3.339940	10.319984	-1.755575
16	6	0	4.269732	6.129216	0.068495
17	6	0	3.593038	4.959593	0.453797
18	6	0	4.225201	3.722020	0.440586

19	6	0	5.565219	3.591001	0.038637
20	6	0	6.245735	4.761246	-0.337625
21	6	0	5.612987	6.000701	-0.323036
22	1	0	2.548672	5.018424	0.746249
23	1	0	3.674842	2.841939	0.760533
24	1	0	7.278527	4.696402	-0.668589
25	1	0	6.173918	6.886186	-0.608760
26	6	0	0.000000	11.284498	0.005127
27	6	0	-0.596437	12.555555	0.035630
28	6	0	0.162665	13.722445	-0.005404
29	1	0	-1.680905	12.619527	0.058408
30	1	0	-0.329613	14.691042	0.011450
31	6	0	-0.888513	10.087982	-0.013409
32	6	0	-1.915392	9.941021	0.932240
33	6	0	-2.754683	8.829224	0.919080
34	6	0	-2.608063	7.820986	-0.047224
35	6	0	-1.599043	7.986857	-1.012179
36	6	0	-0.757272	9.092396	-0.994713
37	1	0	-2.034073	10.691663	1.709321
38	1	0	-3.508465	8.723049	1.694282
39	1	0	-1.486652	7.247963	-1.800428
40	1	0	0.009544	9.191784	-1.756544
41	6	0	-3.462740	6.609537	-0.039024
42	6	0	-4.817407	6.659469	0.330315
43	6	0	-5.602628	5.510587	0.352251
44	6	0	-5.070229	4.257109	0.006291
45	6	0	-3.717394	4.209644	-0.370747
46	6	0	-2.933255	5.356781	-0.391848
47	1	0	-5.265945	7.614283	0.590347
48	1	0	-6.641186	5.583298	0.662981
49	1	0	-3.278159	3.261471	-0.667327
51	6	0	8.989853	-6.823590	-0.047943
52	6	0	9.644316	-8.064905	-0.101388
53	6	0	11.033474	-8.162251	-0.082941
54	1	0	9.041492	-8.968632	-0.124040
55	1	0	11.509807	-9.138313	-0.117261
56	6	0	7.500016	-6.812390	-0.008277
57	6	0	6.798036	-6.127978	0.996784
58	6	0	5.408756	-6.132237	1.031784
59	6	0	4.654907	-6.814607	0.060746
60	6	0	5.358222	-7.519507	-0.929459
61	6	0	6.750910	-7.522220	-0.959637
62	1	0	7.349862	-5.592633	1.763086
63	1	0	4.898375	-5.613726	1.838353
64	1	0	4.809310	-8.038235	-1.710465
65	1	0	7.267398	-8.052465	-1.755575
66	6	0	3.173190	-6.762304	0.068495
67	6	0	2.498615	-5.591458	0.453797
68	6	0	1.110763	-5.520141	0.440586
69	6	0	0.327288	-6.615122	0.038637
70	6	0	1.000492	-7.789588	-0.337625
71	6	0	2.390266	-7.861340	-0.323036
72	1	0	3.071747	-4.716426	0.746249
73	1	0	0.623771	-4.603477	0.760533
74	1	0	0.427940	-8.651590	-0.668589
75	1	0	2.876653	-8.789863	-0.608760
76	6	0	9.772662	-5.642249	0.005127
77	6	0	11.171648	-5.761248	0.035630

78	6	0	11.802654	-7.002094	-0.005404
79	1	0	11.769283	-4.854057	0.058408
80	1	0	12.887622	-7.060068	0.011450
81	6	0	9.180705	-4.274517	-0.013409
82	6	0	9.566873	-3.311733	0.932240
83	6	0	9.023674	-2.028986	0.919080
84	6	0	8.077204	-1.651844	-0.047224
85	6	0	7.716343	-2.608617	-1.012179
86	6	0	8.252882	-3.890381	-0.994713
87	1	0	10.276288	-3.584272	1.709321
88	1	0	9.308615	-1.323105	1.694282
89	1	0	7.020246	-2.336503	-1.800428
90	1	0	7.955546	-4.604158	-1.756544
91	6	0	7.455397	-0.305947	-0.039024
92	6	0	8.175973	0.842263	0.330315
93	6	0	7.573622	2.096725	0.352251
94	6	0	6.221879	2.262392	0.006291
95	6	0	5.504356	1.114536	-0.370747
96	6	0	6.105736	-0.138117	-0.391848
97	1	0	9.227135	0.753301	0.590347
98	1	0	8.155871	2.959787	0.662981
99	1	0	4.463596	1.208233	-0.667327
100	1	0	5.514083	-1.006309	-0.667478
101	6	0	-10.404329	-4.373646	-0.047943
102	6	0	-11.806571	-4.319770	-0.101388
103	6	0	-12.585454	-5.474144	-0.082941
104	1	0	-12.287809	-3.345846	-0.124040
105	1	0	-13.668915	-5.398629	-0.117261
106	6	0	-9.649711	-3.089009	-0.008277
107	6	0	-8.706003	-2.823283	0.996784
108	6	0	-8.015051	-1.618002	1.031784
109	6	0	-8.229076	-0.623964	0.060746
110	6	0	-9.191195	-0.880603	-0.929459
111	6	0	-9.889888	-2.085350	-0.959637
112	1	0	-8.518293	-3.568851	1.763086
113	1	0	-7.310816	-1.435254	1.838353
114	1	0	-9.365971	-0.145867	-1.710465
115	1	0	-10.607338	-2.267519	-1.755575
116	6	0	-7.442922	0.633089	0.068495
117	6	0	-6.091652	0.631865	0.453797
118	6	0	-5.335964	1.798121	0.440586
119	6	0	-5.892508	3.024121	0.038637
120	6	0	-7.246227	3.028342	-0.337625
121	6	0	-8.003253	1.860638	-0.323036
122	1	0	-5.620418	-0.301997	0.746249
123	1	0	-4.298613	1.761537	0.760533
124	1	0	-7.706467	3.955188	-0.668589
125	1	0	-9.050571	1.903677	-0.608760
126	6	0	-9.772662	-5.642249	0.005127
127	6	0	-10.575211	-6.794307	0.035630
128	6	0	-11.965318	-6.720351	-0.005404
129	1	0	-10.088378	-7.765470	0.058408
130	1	0	-12.558010	-7.630974	0.011450
131	6	0	-8.292193	-5.813466	-0.013409
132	6	0	-7.651481	-6.629289	0.932240
133	6	0	-6.268991	-6.800238	0.919080
134	6	0	-5.469141	-6.169142	-0.047224
135	6	0	-6.117300	-5.378241	-1.012179

136	6	0	-7.495610	-5.202015	-0.994713
137	1	0	-8.242215	-7.107390	1.709321
138	1	0	-5.800150	-7.399945	1.694282
139	1	0	-5.533594	-4.911459	-1.800428
140	1	0	-7.965091	-4.587626	-1.756544
141	6	0	-3.992657	-6.303590	-0.039024
142	6	0	-3.358565	-7.501731	0.330315
143	6	0	-1.970994	-7.607312	0.352251
144	6	0	-1.151650	-6.519501	0.006291
145	6	0	-1.786961	-5.324180	-0.370747
146	6	0	-3.172481	-5.218664	-0.391848
147	1	0	-3.961189	-8.367584	0.590347
148	1	0	-1.514685	-8.543085	0.662981
149	1	0	-1.185438	-4.469705	-0.667327
150	1	0	-3.628531	-4.272181	-0.667478

Calculated at B3LYP/6-31G(d) level