Supporting Information

Individually separated supramolecular polymer chains toward solution processable supramolecular polymeric materials

Takuma Shimada,[1,2] Yuichiro Watanabe,[3] Takashi Kajitani,[4] Masayuki Takeuchi,[2]

Yutaka Wakayama,[1,2] Kazunori Sugiyasu[3]*

[1] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Nishi-ku, Fukuoka 819-0395, Japan

[2] National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan

[3] Department of Polymer Chemistry, Kyoto University, Kyotodaigaku-katsura, Kyoto 615-8510, Japan

[4] Open Facility Development Office, Open Facility Center, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.

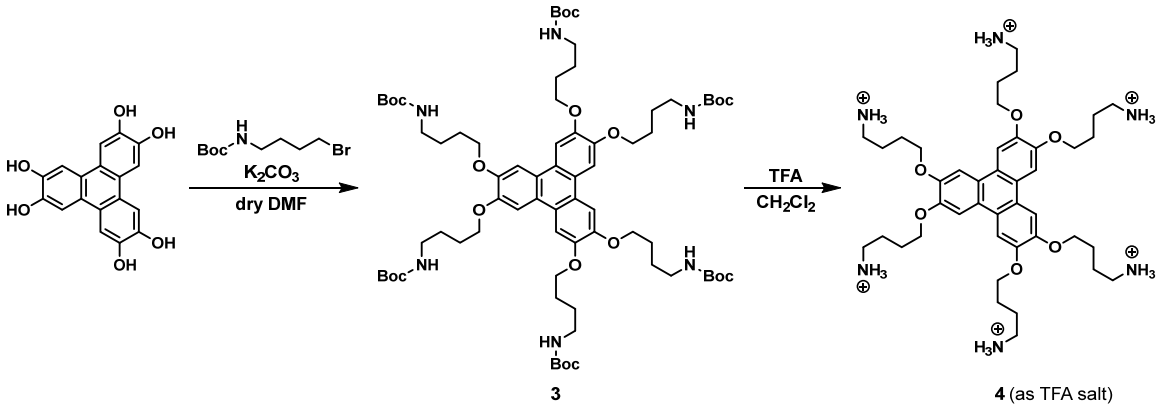
sugiyasu.kazunori.8z@kyoto-u.ac.jp

Table of Contents

General Methods

Air and water sensitive synthetic manipulations were performed under a nitrogen or an argon atmosphere using standard Schlenk techniques. Chemicals were purchased from Aldrich, TCI, Kanto Chemical, or Fujifilm Wako and used as received without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL, ECS-400 (400 MHz) and an ECZ400S (400 MHz) spectrometer using tetramethylsilane (0 ppm for ^{1}H NMR) or residual $CHCl_3$ (77 ppm for ^{13}C NMR) as an internal standard. $CDCl_3$ and DMSO-d_6 were purchased from Kanto Chemical or Eurisotop. Splitting patterns are designated as s, singlet; d, doublet; m, multiplet; t, triplet; q, quartet; br, broad. Gel permeation chromatography (GPC) was performed using a Japan Analytical Industry, LC-5060P equipped with JAIGEL-2.5HR Plus column and JAIGEL-2HR Plus column (eluent: $CHCl_3$) and a UV detector. Scanning Electron Microscopy (SEM) measurements were performed on a HITACHI, FE-SEM: SU8220. Samples were mounted on conducting carbon tape attached to a SEM stage, and then coated with platinum. The images were recorded with an operating voltage of 1.0 kV. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained using a Bruker Daltonics, ultrafleXtreme (Laser: 337 nm) with dithranol as a matrix. Electrospray ionization (ESI) mass spectra were obtained using a Thermo Fisher Scientific Exactive Plus. Polarized optical microscopy (POM) were performed on a Nikon ECLIPSE E600 POL. Atomic force microscopy (AFM) was performed on a Bruker, model MultiMode 8 atomic force microscope under ambient conditions in the scan assist mode. AFM images were analyzed by Bruker, Nanoanalysis. Powder X-ray diffraction (XRD) experiment was carried out on the Rigaku, NANO-Viewer equipped with a Dectris, Pilatus100k detector, and wavelength of the X-ray beam is 1.541 Å. The position of incident X-ray beam on the detector were calibrated using silver behenate. Grazing incidence wide-angle X-ray diffraction (GI-WAXD) experiment was carried out on the Rigaku, NANOPIX equipped with a Rigaku, HyPix-6000 detector, and wavelength of the X-ray beam is 1.541 Å. The position of incident X-ray beam on the detector were calibrated using silver behenate. The sample was placed on Si substrate.

Synthesis and Characterization



Scheme S1. Synthetic route of Triphenylene derivative **4**.

Synthesis of 3

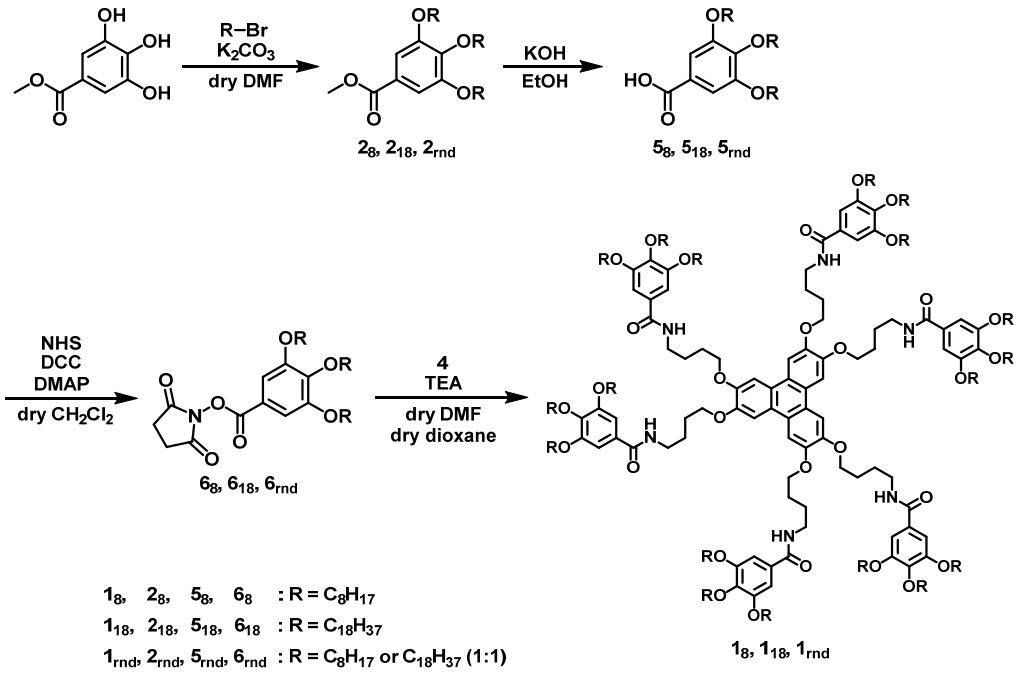
2,3,6,7,10,11-Hexahydroxytriphenylene (0.294 g, 0.91 mmol), *tert*-butyl *N*-(4-bromobutyl)carbamate (1.65 g, 6.54 mmol), K_2CO_3 (2.60 g, 18.8 mmol) were dissolved in dry *N*,*N*-dimethylformamide (DMF) (22 mL). After stirring for 24 h at 70 °C, the reaction mixture was poured into water and extracted with ethyl acetate. The organic phase was washed with brine, then dried with $MgSO_4$ (anhydrous). The filtrate was evaporated, and the solid residue was purified with flash chromatography on silica gel using dichloromethane/ethyl acetate (2:1) as eluent. The obtained solid was further purified by reprecipitation with dichloromethane/*n*-hexane to give **3** (0.871 g, 71%) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78 (s, 6H), 4.93 (s^{br}, 6H), 4.25 (t, J = 6.0 Hz, 12H), 3.26 (q, J = 6.1 Hz, 12H), 1.98 (quin, J = 6.6 Hz, 12H), 1.78 (quin, J = 7.0 Hz, 12H), 1.43 (s, 54H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.2, 148.7, 123.6, 106.6, 79.1, 69.1, 40.4, 28.6, 27.2, 26.6. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{72}H_{114}N_6O_{18}$ 1373.8082 found 1373.8026.

Synthesis of 4

To a solution of compound **3** (2.12 g, 1.6 mmol) in dichloromethane (50 mL) was added trifluoroacetic acid (TFA) (6.5 mL, 85 mmol). After stirring for 5 h at room temperature, a small amount of methanol, followed by a large amount of dichloromethane were added to give a precipitate. The precipitate was collected by filtration and dried *in vacuo* to give **4** (2.19 g, 97% yield as a TFA salt) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.00 (s, 6H), 7.88 (br, 18H), 4.27 (t, J = 5.8 Hz, 12H), 2.96 (t, J = 7.6 Hz, 12H), 1.93–1.87 (m, 12H), 1.84–1.77 (m, 12H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 158.9, 148.8, 123.5, 107.5, 68.8, 39.3, 26.4, 24.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{42}H_{66}N_6O_6$ 751.5117 found 751.5089.



Scheme S2. Synthetic route of monomers $\mathbf{1_8}$, $\mathbf{1_{18}}$, $\mathbf{1_{rnd}}$.

Compound $\mathbf{2_8}$, $\mathbf{5_8}$, $\mathbf{2_{18}}$, $\mathbf{5_{18}}$ were synthesized following similar procedure to the literature[S1].

Synthesis of $\mathbf{2_{rnd}}$

To a mixture of methyl 3,4,5-trihydroxybenzoate (methyl gallate) (5.00 g, 27.2 mmol) and K_2CO_3 (26.3 g, 190 mmol) in dry DMF (80 mL) were added 1-bromooctane (10.5 g, 54.3 mmol) and 1-bromooctadecane (18.1 g, 54.3 mmol) under an argon atmosphere. After stirring overnight at 70 °C, the reaction mixture was filtered. The filtrate was extracted with hexane, and the organic phase was washed with water, then dried with Na_2SO_4 (anhydrous). The filtrate was chromatographed on silica gel using dichloromethane/*n*-hexane (1:1) as eluent to give $\mathbf{2_{rnd}}$ (yellow oil, 21.0 g, quant.) as a mixture of six distinct compounds.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.25 (s, 2H), 4.02–3.99 (m, 6H), 3.89 (s, 3H), 1.85–1.70 (m, 6H), 1.528–1.407 (m, 6H), 1.39–1.181 (m, 55H), 0.90–0.86 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.0, 152.8, 142.3, 124.6, 107.9, 73.5, 69.1, 52.1, 31.9, 31.8, 30.3, 29.7, 29.6, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{32}H_{56}O_5$ 543.4020 found 543.3997, $[M + Na]^+$ Calcd. for $C_{42}H_{76}O_5$ 683.5585 found 683.5555, $[M + Na]^+$ Calcd. for $C_{52}H_{96}O_5$ 823.7150 found 823.7114, $[M + Na]^+$ Calcd. for $C_{62}H_{116}O_5$ 963.8715 found 963.8667.

Synthesis of $\mathbf{5_{rnd}}$

To a solution of $\mathbf{2_{rnd}}$ (21.0 g, 28.7 mmol) in ethanol (280 mL) was added KOH (20.4 g, 364 mmol). After stirring for 4 h at 80 °C, the reaction mixture was poured into 1 M HCl aq. (400 mL), and the precipitate was filtered. The solid was washed with water and methanol and then dried *in vacuo* to give a pale orange solid $\mathbf{5_{rnd}}$ (19.1 g, 92%) as a mixture of six distinct compounds.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.21 (s, 2H), 6.39 (s^{br}, 1H), 3.98 (t, J = 6.6 Hz, 2H), 3.93 (t, J = 6.4 Hz, 4H), 1.79–1.71 (m, 6H), 1.50–1.39 (m, 6H), 1.33–1.22 (m, 53H), 0.89–0.86 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 171.6, 152.6, 141.9, 126.2, 108.0, 73.4, 69.0, 31.9, 31.8, 30.4, 29.8, 29.7, 29.6, 29.5, 29.4, 29.4, 29.4, 26.2, 26.1, 22.7, 14.1. HRMS (ESI) *m/z*: $[M - H]^-$ Calcd. for $C_{31}H_{54}O_5$ 505.3888 found 505.3893, $[M - H]^-$ Calcd. for $C_{41}H_{74}O_5$ 645.5453 found 645.5453, $[M - H]^-$ Calcd. for $C_{51}H_{94}O_5$ 785.7018 found 785.7019, $[M - H]^-$ Calcd. for $C_{61}H_{114}O_5$ 925.8583 found 925.8583.

Synthesis of $\mathbf{6_{rnd}}$

A mixture of $\mathbf{5_{rnd}}$ (9.96 g, 13.9 mmol), *N*-hydroxysuccinimide (NHS) (3.23 g, 28.0 mmol), *N*,*N*′-Dicyclohexylcarbodiimide (DCC) (3.74 g, 18.1 mmol) and 4-dimethylaminopyridine (DMAP) (0.173 g, 1.4 mmol) were dissolved in dry dichloromethane (20 mL). After stirring overnight at room temperature, the reaction mixture was filtered. The filtrate was extracted with dichloromethane and washed with brine. the organic phase was separated, then dried with Na_2SO_4 (anhydrous). After filtration on silica gel, the filtrate was evaporated to give a pale yellow solid $\mathbf{6_{rnd}}$ (10.7 g, 95%) as a mixture of six distinct compounds with trace amount of unreacted DCC. The mixture was used without further purification in order not to change the statistical compositions of the mixture.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33 (s, 2H), 4.04 (t, J = 6.6 Hz, 2H), 4.01 (t, J = 6.4 Hz, 4H), 2.91–2.90 (m, 4H), 1.85–1.70 (m, 6H), 1.52–1.41 (m, 6H), 1.39–1.22 (m, 56H), 0.90–0.86 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.3, 161.7, 153.1, 144.1, 119.0, 108.9, 73.6, 69.2, 31.9, 31.8, 30.3, 29.7, 29.6, 29.5, 29.5, 29.3, 29.3, 29.2, 29.2, 26.0, 25.6, 22.7, 22.6, 14.1. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{35}H_{57}NO_7$ 626.4027 found 626.3998, $[M + Na]^+$ Calcd. for $C_{45}H_{77}NO_7$ 766.5592 found 766.5556, $[M + Na]^+$ Calcd. for $C_{55}H_{97}NO_7$ 906.7157 found 906.7113, $[M + Na]^+$ Calcd. for $C_{65}H_{117}NO_7$ 1046.8722 found 1046.8722.

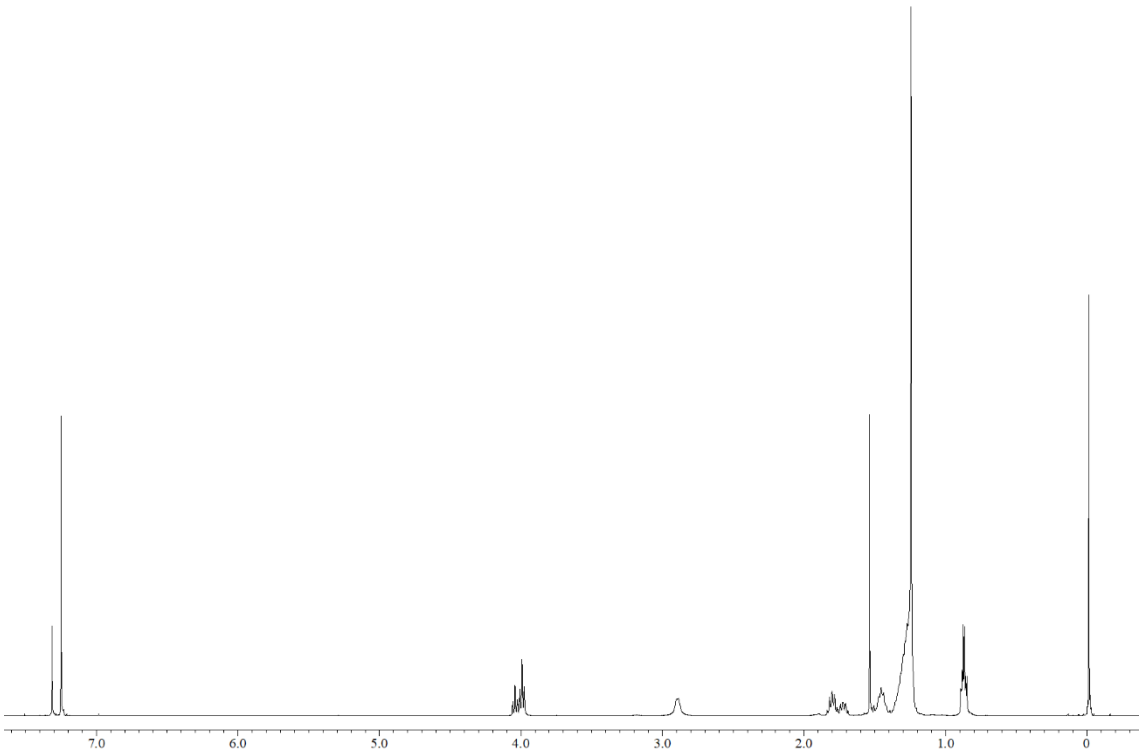


Figure S1. ^{1}H NMR spectrum of $\mathbf{6_{rnd}}$ in $CDCl_3$ at 298 K.

Synthesis of 6_8

To a mixture of $\mathbf{5_8}$ (10.0 g, 19.8 mmol), NHS (4.56 g, 39.6 mmol) and DMAP (0.254 g, 2.1 mmol) in dry dichloromethane (25 mL) was added DCC (5.30 g, 25.7 mmol). After stirring overnight at room temperature, the reaction mixture was filtered. The filtrate was washed with brine and the organic phase was separated and dried with Na_2SO_4 (anhydrous). The crude product was chromatographed on silica gel using dichloromethane as eluent to give $\mathbf{6_8}$ (11.5 g, 96%) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33 (s, 2H), 4.06 (t, J = 6.8 Hz, 2H), 4.01 (t, J = 6.4 Hz, 4H), 2.91 (s, 2H), 2.90 (s, 2H), 1.85–1.70 (m, 6H), 1.50–1.29 (m, 30H), 0.90–0.87 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.5, 161.8, 153.2, 144.2, 119.2, 109.0, 73.7, 69.3, 32.0, 31.9, 30.4, 29.5, 29.4, 29.4, 29.3, 29.3, 26.1, 25.8, 22.7, 14.2. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{35}H_{57}NO_7$ 626.4027 found 626.4000.

Synthesis of 6_{18}

To a mixture of $\mathbf{5_{18}}$ (3.00 g, 3.2 mmol), NHS (0.754 g, 6.6 mmol), DMAP (0.0428 g, 0.35 mmol) in dry dichloromethane (8 mL) was added DCC (0.866 g, 4.2 mmol). Then, target compound $\mathbf{6_{18}}$ was synthesized following similar procedure to $\mathbf{6_8}$ as a white solid (1.80 g, 54%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.32 (s, 2H), 4.05 (t, J = 6.8 Hz, 2H), 4.00 (t, J = 6.8 Hz, 4H), 2.92 (s, 2H), 2.90 (s, 2H), 1.85–1.70 (m, 6H), 1.42–1.18 (m, 90H), 0.90–0.86 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.3, 161.7, 153.1, 144.1, 119.1, 108.9, 73.7, 69.3, 31.9, 30.3, 29.7, 29.6, 29.5, 29.4, 29.2, 26.0, 25.7, 22.7, 14.1. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{65}H_{117}NO_7$ 1046.8722 found 1046.8643.

Synthesis of $\mathbf{1_{rnd}}$

To a solution of triphenylene derivative **4** (0.523 g, 0.36 mmol) in dry DMF (50 mL) under a N_2 atmosphere was added triethylamine (1.5 mL, 10.8 mmol). Then, the mixture was added to NHS ester $\mathbf{6_{rnd}}$ (1.96 g, 2.4 mmol) in dry dioxane (30 mL). After stirring for 24 h at 80 °C, the reaction mixture was poured into water, and then, the precipitate was filtered. The residue was purified by column chromatography using chloroform/acetone (19:1) as eluent. The product was further purified with GPC ($CHCl_3$ as eluent) and reprecipitated with dichloromethane/methanol to give $\mathbf{1_{rnd}}$ as a white solid (1.46 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (s, 6H), 7.24 (br, 6H), 7.08 (s, 12H), 4.25–4.22 (m, 12H), 3.93 (t, J = 6.8 Hz, 12H), 3.88–3.84 (m, 24H), 3.52–3.47 (m, 12H), 1.97–1.85 (m, 24H), 1.75–1.63 (m, 36H), 1.47–1.22 (m, 372H), 0.88–0.81 (m, 55H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.4, 153.0, 148.5, 140.8, 129.4, 123.5, 106.2, 105.6, 73.5, 69.1, 40.0, 31.9, 31.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 27.0, 26.1, 26.1, 22.7, 14.1. HRMS (ESI)[S2] *m/z*: $[M + 2Na]^{2+}$ Calcd. for $C_{288}H_{498}N_6O_{30}$ 2283.8706 found 2283.8804, $[M + 2Na]^{2+}$ Calcd. for $C_{298}H_{518}N_6O_{30}$ 2353.94885 found 2353.9641, $[M + 2Na]^{2+}$ Calcd. for $C_{308}H_{538}N_6O_{30}$ 2424.0271 found 2424.0178, $[M + 2Na]^{2+}$ Calcd. for $C_{318}H_{558}N_6O_{30}$ 2494.10535 found 2494.1162, $[M + 2Na]^{2+}$ Calcd. for $C_{328}H_{578}N_6O_{30}$ 2564.1836 found 2564.1646.

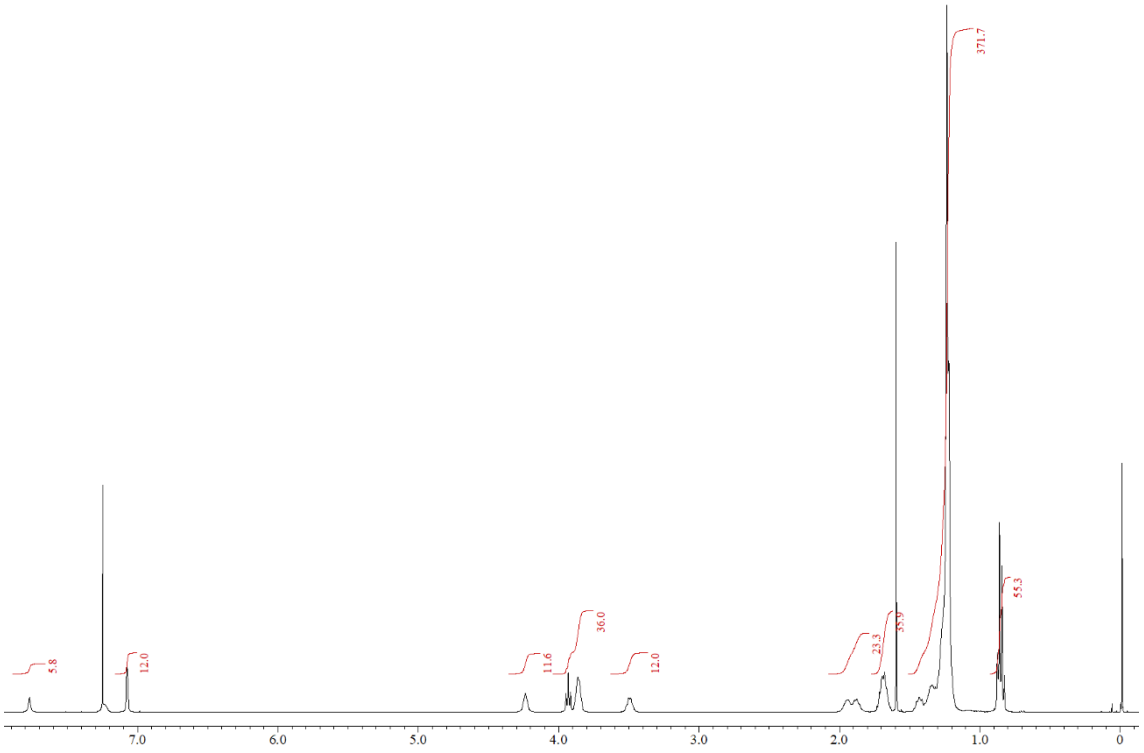


Figure S2. ^{1}H NMR spectrum of $\mathbf{1_{rnd}}$ in $CDCl_3$ at 298 K[S3].

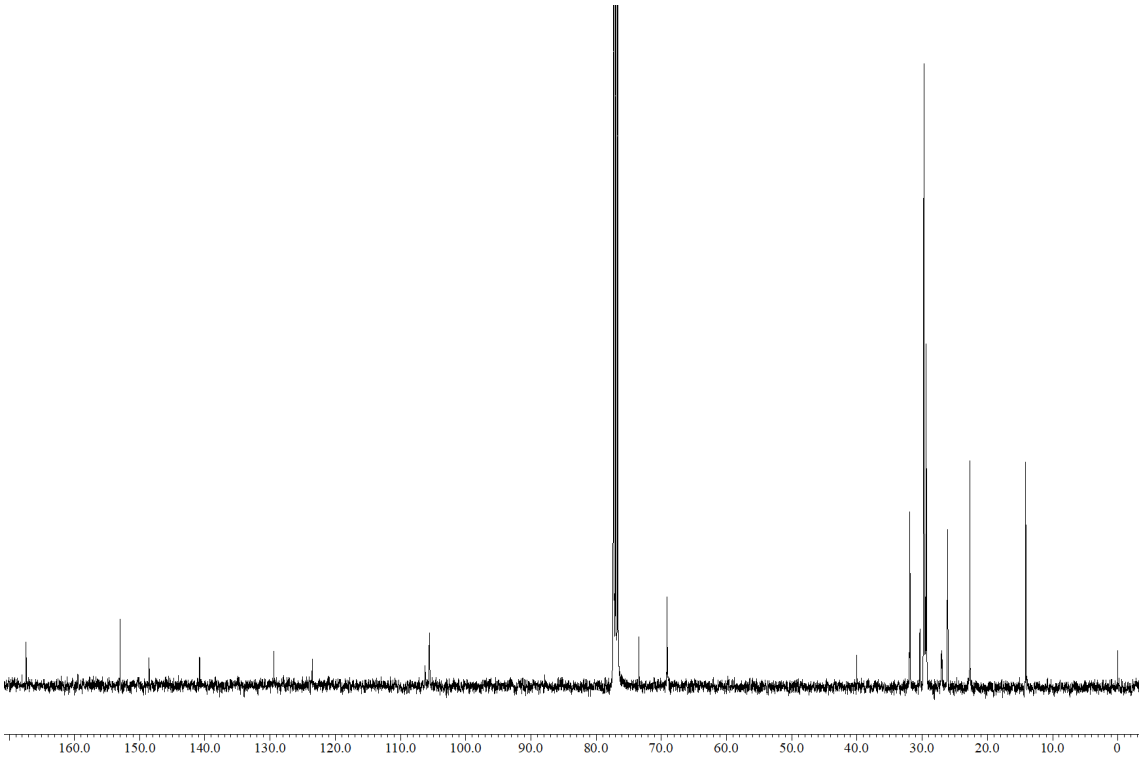


Figure S3. ^{13}C NMR spectrum of $\mathbf{1_{rnd}}$ in $CDCl_3$ at 298 K.

Synthesis of $\mathbf{1_8}$

To a solution of triphenylene derivative **4** (0.306 g, 0.21 mmol) in dry DMF (15 mL) under a N_2 atmosphere was added triethylamine (0.9 mL, 6.5 mmol). Then, the mixture was added to NHS ester $\mathbf{6_8}$ (0.800 g, 1.3 mmol) in dry dioxane (30 mL). Target compound $\mathbf{1_8}$ was obtained following the similar procedure to $\mathbf{1_{rnd}}$ as a white solid (0.486 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (s, 6H), 7.21 (t, J = 5.8 Hz, 6H), 7.08 (s, 12H), 4.25 (t, J = 5.2 Hz, 12H), 3.95 (t, J = 6.6 Hz, 12H), 3.87 (t, J = 6.6 Hz, 24H), 3.51 (q, J = 6.2 Hz, 12H), 1.99–1.85 (m, 24H), 1.75–1.66 (m, 36H), 1.48–1.233 (m, 180H), 0.89–0.84 (m, 54H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.4, 153.0, 148.5, 140.8, 129.4, 123.5, 106.2, 105.6, 73.4, 69.1, 40.0, 31.9, 31.8, 30.3, 29.5, 29.4, 29.3, 27.1, 27.0, 26.1, 22.7, 14.1. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{228}H_{378}N_6O_{30}$ 3703.813 found 3703.8203.

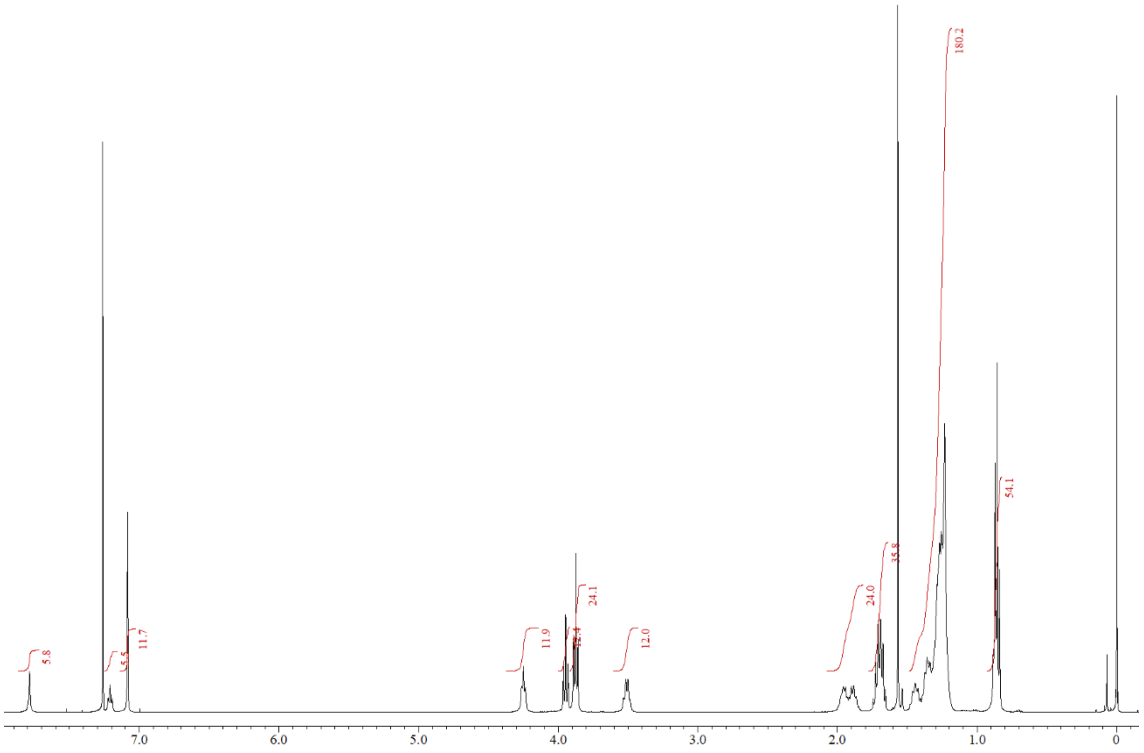


Figure S4. ^{1}H NMR spectrum of $\mathbf{1_8}$ in $CDCl_3$ at 298 K.

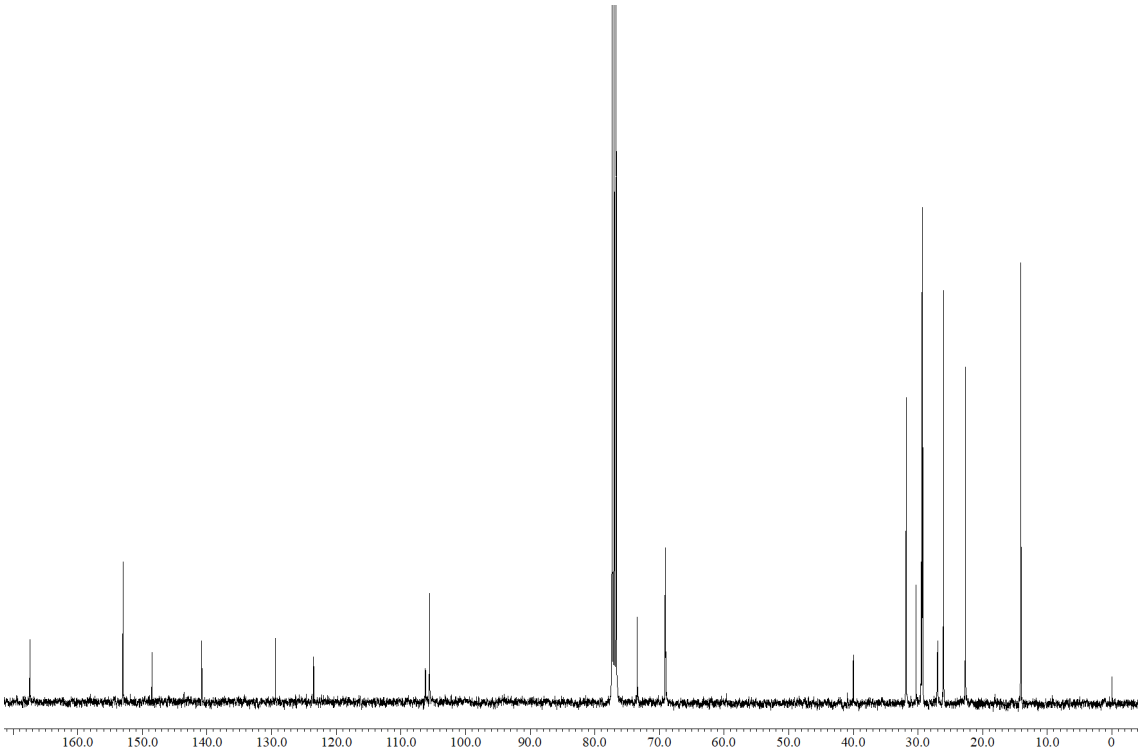


Figure S5. ^{13}C NMR spectrum of $\mathbf{1_8}$ in $CDCl_3$ at 298 K.

Synthesis of $\mathbf{1_{18}}$

To a solution of triphenylene derivative **4** (0.102 g, 0.075 mmol) in dry DMF (10 mL) under a N2 atmosphere was added triethylamine (0.31 mL, 2.2 mmol). Then, NHS ester $\mathbf{6_{18}}$ (0.537 g, 0.52 mmol) and dry dioxane (5 mL). Target compound $\mathbf{1_{18}}$ was obtained following the similar procedure to $\mathbf{1_{rnd}}$ as a white solid (0.321 g, 69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79 (s, 6H), 7.26–7.23 (m, 6H), 7.09 (s, 12H), 4.26–4.24 (m, 12H), 3.94 (t, J = 6.4 Hz, 12H), 3.87 (t, J = 6.4 Hz, 24H), 3.53–3.48 (m, 12H), 1.98–1.85 (m, 24H), 1.75–1.66 (m, 36H), 1.48–1.17 (m, 540H), 0.89–86 (m, 54H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.5, 153.0, 148.6, 140.9, 129.5, 123.6, 106.4, 105.6, 73.5, 69.2, 40.1, 32.0, 30.4, 29.9, 29.6, 29.5, 27.2, 27.1, 26.2, 22.8, 14.2. HRMS (ESI) *m/z*: $[M + 2Na]^{2+}$ Calcd. for $C_{408}H_{738}N_6O_{30}$ 3126.8163 found 3126.8149[S4].

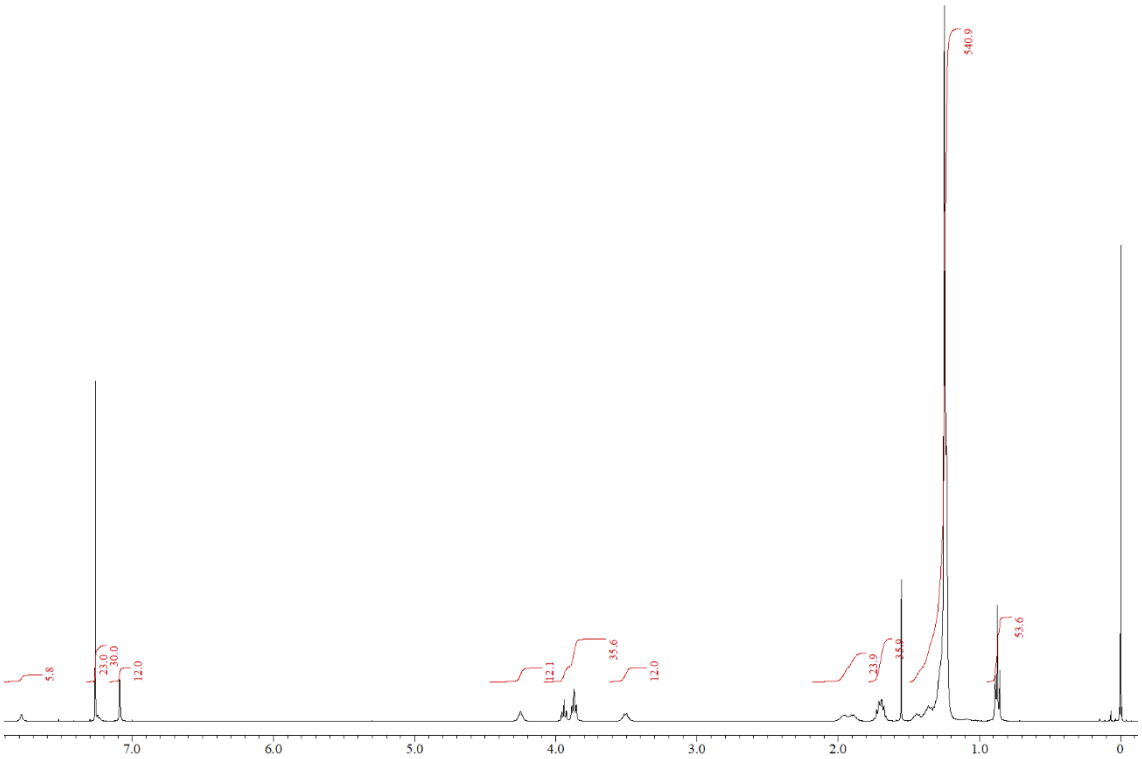


Figure S6. ^{1}H NMR spectrum of $\mathbf{1_{18}}$ in $CDCl_3$ at 298 K.

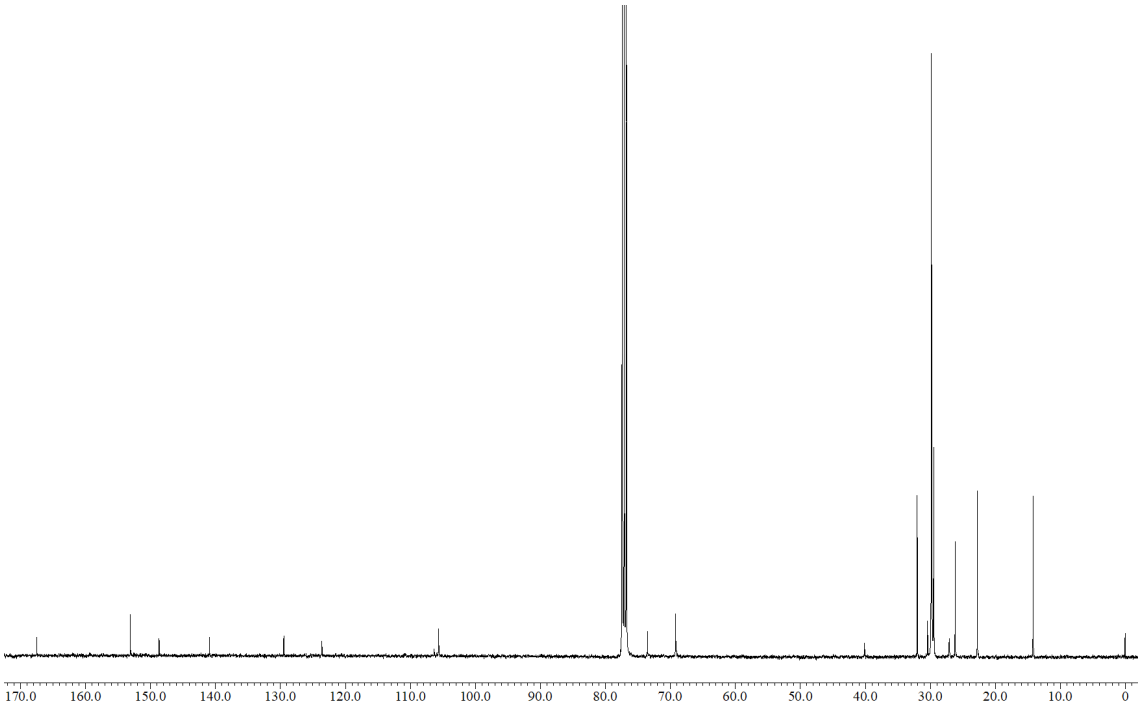


Figure S7. ^{13}C NMR spectrum of $\mathbf{1_{18}}$ in $CDCl_3$ at 298 K.

Note and reference

S1 D. H. Wang, Z. Shen, M. Guo, S. Z. D. Cheng and F. W. Harris, *Macromolecules*, 2007, **40**, 889–900.

S2 Among the 18 different molecular weight of the monomers, the five most strongly detected peaks were used for identification.

S3 Sum of the integration values of the protons on the alkyl chains is expected for 486H, found 499H.

S4 Due to the high molecular weight, monoisotopic peaks could not be obtained, and isotopic peaks were used for identification.

Supporting Figures

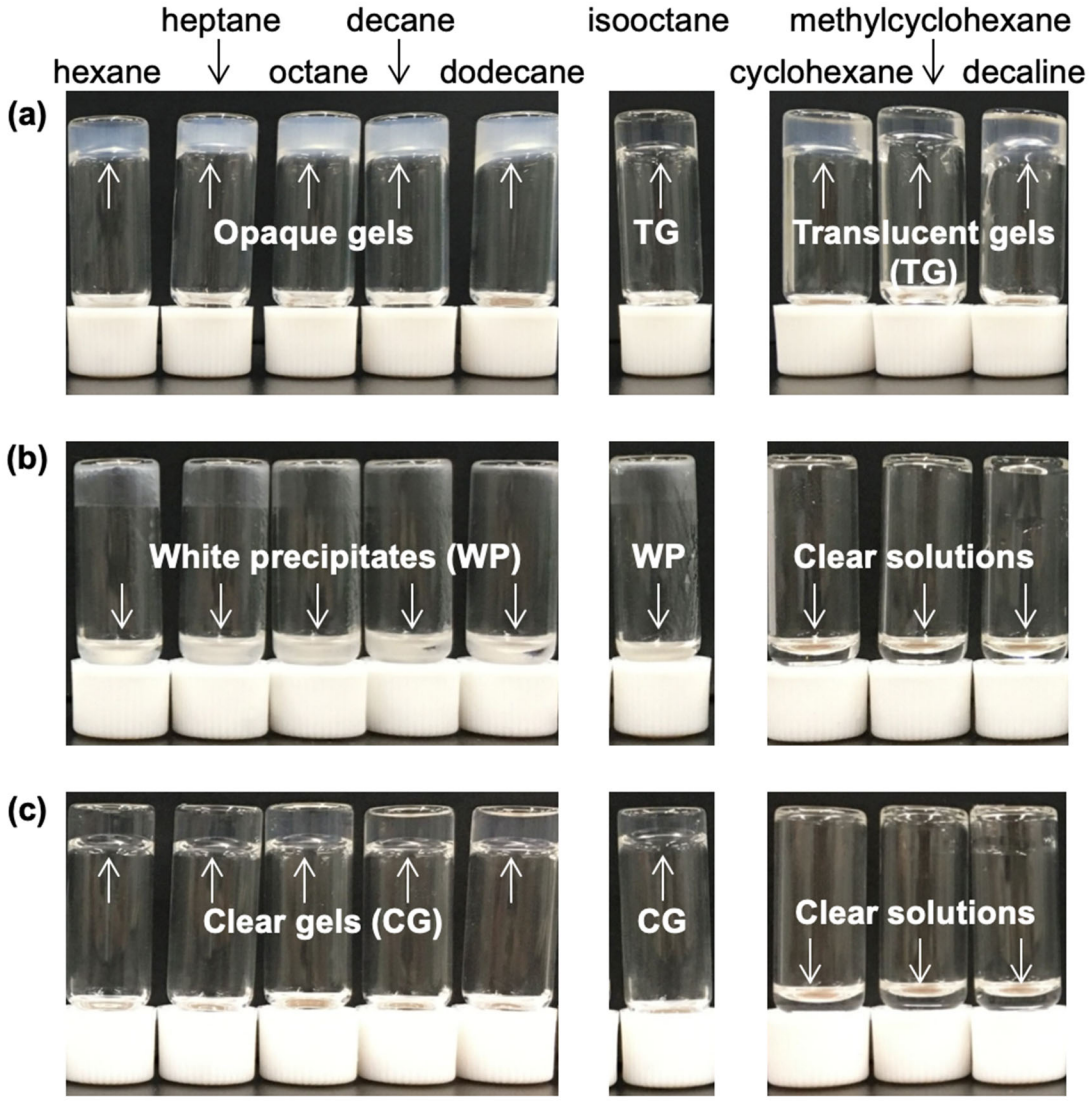


Figure S8. Tube inversion test of concentrated solutions of (a) $\mathbf{1}_{8}$, (b) $\mathbf{1}_{18}$, (c) $\mathbf{1}_{rnd}$ in aliphatic hydrocarbon solvents incubated for several days (1 mM). From left to right, *n*-hexane (nHex), *n*-heptane, *n*-octane, *n*-decane, *n*-dodecane as linear aliphatic solvent, isooctane (iOc) as branched aliphatic solvent and cyclohexane (cHex), methylcyclohexane, decahydronaphthalene (decaline) as cyclic aliphatic solvent.

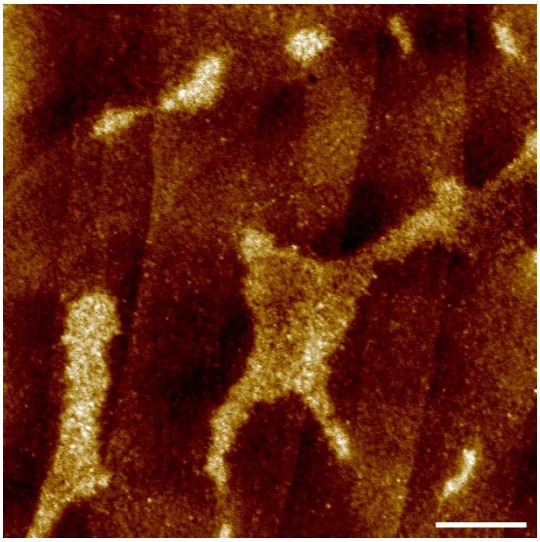


Figure S9. AFM image of $\mathbf{1}_{18}$ in cHex (50 μM) incubated for 2 months, spin-coated on a HOPG substrate (scale bar = 500 nm).

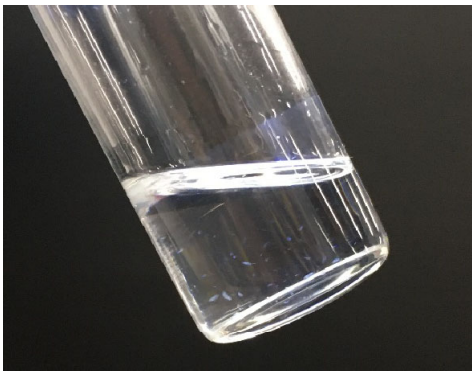


Figure S10. A photograph of the cHex solution of $\mathbf{1}_{8}$ (50 μM) taken 2 days after Fig. 2 (a–c). The solution had been stirred at 400 rpm at room temperature for 2 days. The formation of precipitates in the solution indicates that the bundles were not caused by the drying process.

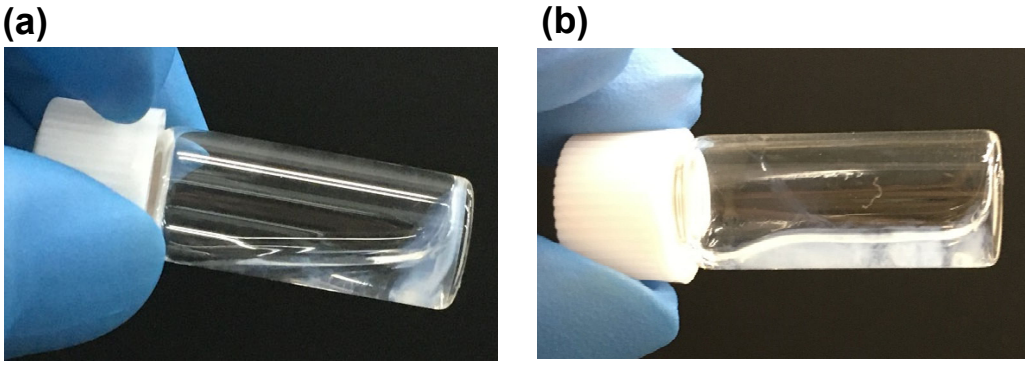


Figure S11. Photographs of (a) nHex gel and (b) iOc gel formed by $\mathbf{1_8}$ after mechanical agitation using vortex mixer for 10 sec.

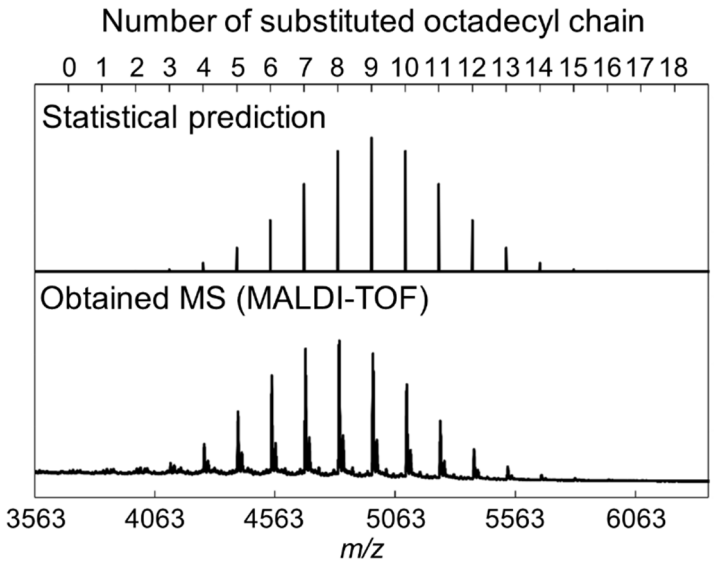


Figure S12. Statistical calculation of molecular weight distribution (above) and obtained MALDI-TOF-MS spectrum (below) of $\mathbf{1_{rnd}}$. (Note that MALDI-TOF-MS sensitivity decreases with the increase in molecular weight.)

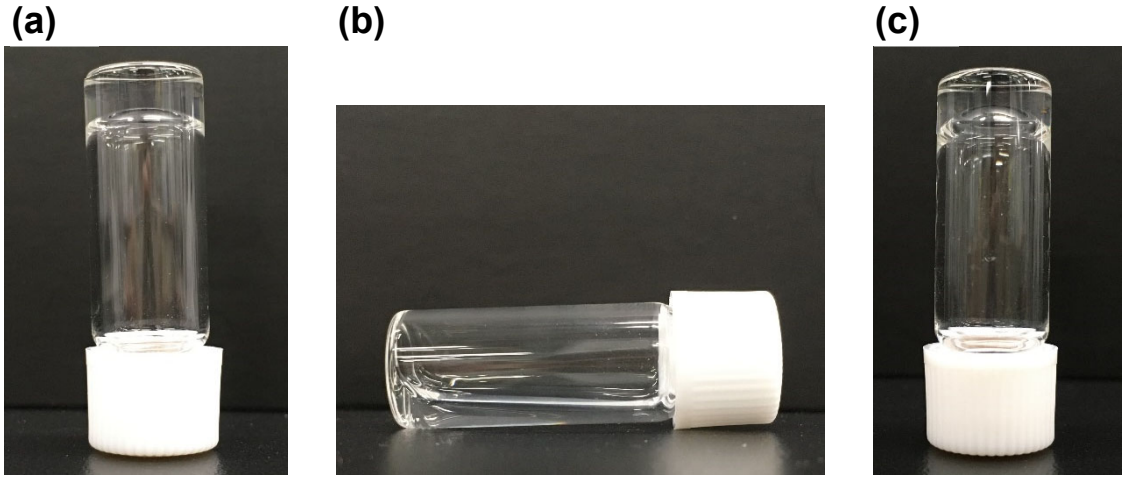


Figure S13. Photographs of (a) nHex gel formed by $\mathbf{1}_{\mathbf{rnd}}$ (1 mM), (b) the same gel which was mechanically agitated using vortex mixer for 10 sec, and (c) the agitated solution which was left for 2 days: the clear gel reformed.

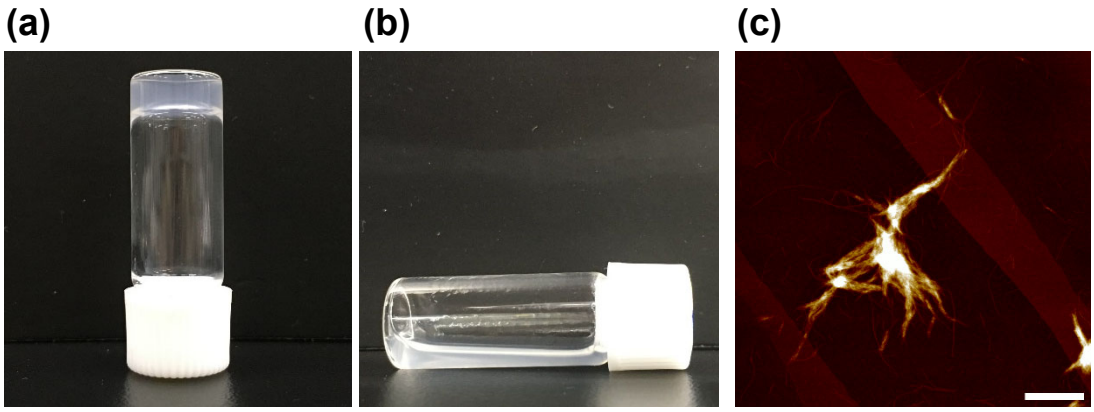


Figure S14. (a) A photograph of nHex gel consisting of a mixture of $\mathbf{1}_{\mathbf{8}}$ and $\mathbf{1}_{\mathbf{18}}$ ([$\mathbf{1}_{\mathbf{8}}$ + $\mathbf{1}_{\mathbf{18}}$ = 1 mM]). (b) A photograph and (c) an AFM image of the same gel which was mechanically agitated using vortex mixer for 10 sec.

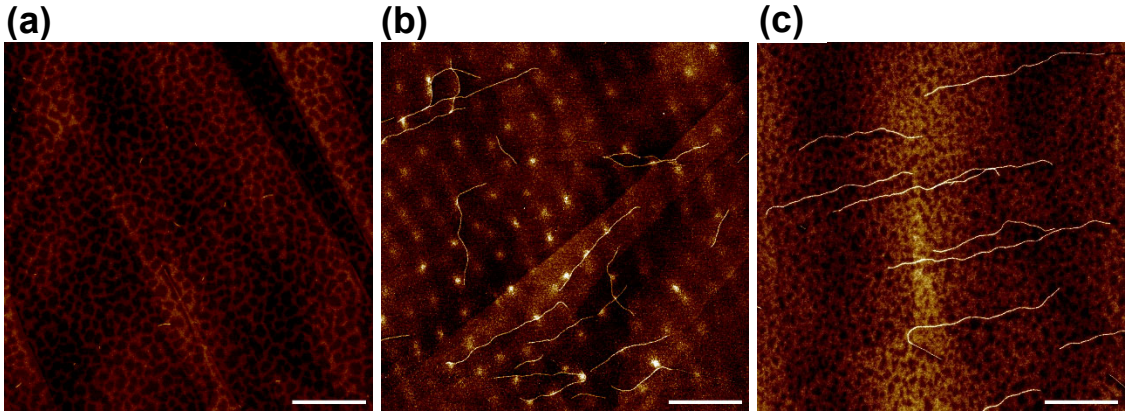


Figure S15. Successive AFM images of seeded polymerization of $\mathbf{1}_{\mathbf{rnd}}$. Supramolecular polymers prepared in iOc (50 μM, Figure 3b) were added as seeds to a cHex solution of $\mathbf{1}_{\mathbf{rnd}}$ (1.2 mM) at a ratio of iOc seed solution : cHex solution = 1 : 5 (v/v) . The images were taken (a) immediately after seeding, (b) 2 hours, and (c) and 4 hours after seeding (scale bar = 1 μm).

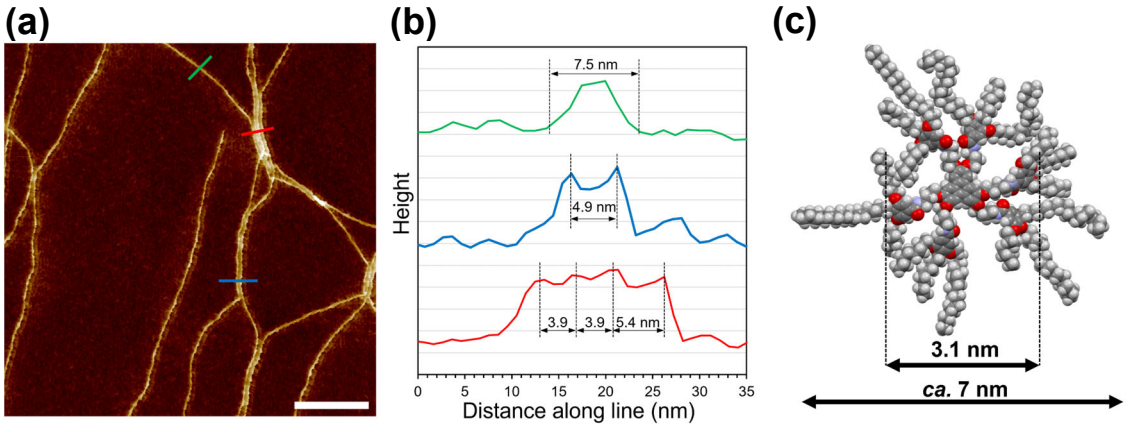


Figure S16. Discussion of the width of individually separated supramolecular polymer chains of $\mathbf{1}_{rnd}$ prepared by seeded supramolecular polymerization in a cHex/iOc mixed solvent (1 mM) described in Fig. 3d. (a) High resolution AFM image of an area where slight bundling occurs; Scale bar = 100 nm. (b) Height measurements across the each coloured line on (a). (c) Computer-generated molecular model of a component of $\mathbf{1}_{rnd}$. Atom colour code: grey, C; red, O; blue, N; white, H.

It is known that the effect called probe-convolution, an inherent feature of AFM, makes objects appear wide depending on the sharpness of the probe. Therefore, when we measure the width of a single supramolecular polymer directly, we would get an 'apparent' value (green line in Figure S16 a,b). However, if the bundled part is measured, the spacing of the supramolecular polymers (that is, width of a supramolecular polymer) can be obtained as an 'actual' value (blue and red line in Figure S16 a,b), and the obtained value corresponds to the diameter of a monomer (Figure S16 c).

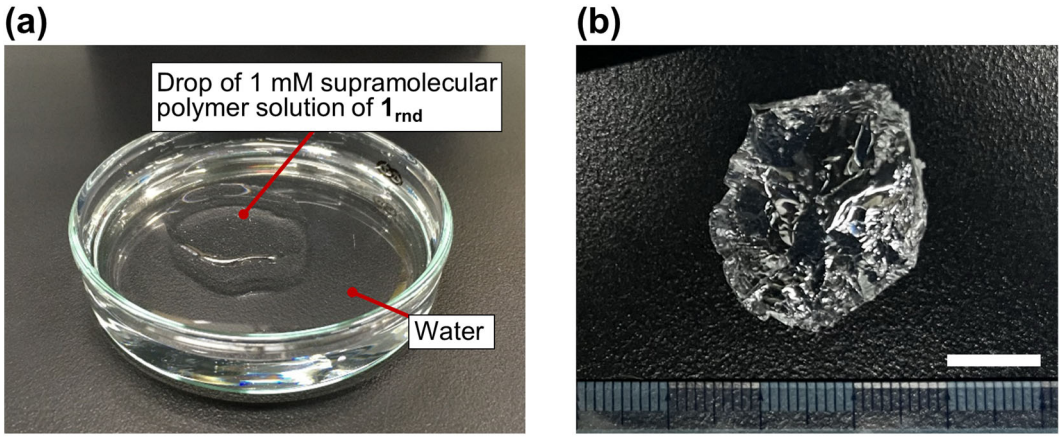


Figure S17. Photographs taken (a) during the preparation of self-standing film and (b) the obtained film; Scale bar = 1 cm. A concentrated solution of supramolecular polymer of $\mathbf{1}_{rnd}$ (1 mM) was drop-casted on a surface of water, and upon drying the organic solvent, the film was formed.

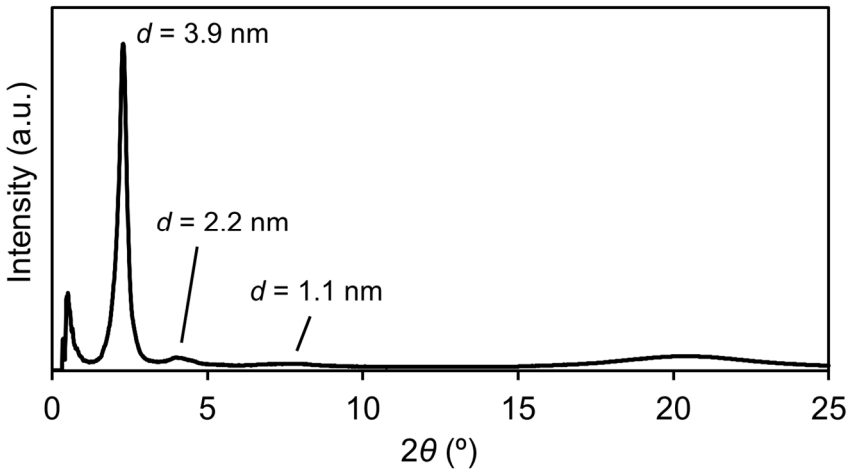


Figure S18. 1D WAXD pattern of $\mathbf{1}_{rnd}$ obtained from 2D GI-WAXD measurement upon exposure to an X-ray beam from the directions parallel to the long axis of the threads.