

Supporting Information for:

Rod-Shaped 1D Polymer-Assisted Anisotropic Self-Assembly of 0D Nanoparticles

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Materials

Fullerene C₆₀ (>99.5%), C₇₀ (>98.0%), tetraphenylethylene (>98.0%), 5,6,11,12-tetraphenylnaphthacene (>99.0%), tetraphenylporphyrin (chlorin free) (>98.0%), 4-cyano-4'-pentylbiphenyl (5CB), 1-octanol, 1-decanol, 3,7-dimethyl-1-octanol, 1-octylamine, 1-decylamine, 1-octanethiol, 1-decanethiol, (-)- β -citronellol, *L*-alanine, pentafluorophenol, triethylene glycol monomethyl ether, *tert*-butyl 4-aminobenzoate, 1-hydroxybenzotriazole monohydrate (HOBt), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC) and ethynylanisole were purchased from Tokyo Chemical Industry and used as received. Superdehydrated *N,N*-Dimethylformamide (DMF), superdehydrated tetrahydrofuran (THF) and 1,1,2,2-tetrachloroethane were purchased from Wako Pure Chemical Industries and used as received. Toluene, ethylacetate, hexane, dichloromethane (DCM), methanol (MeOH), triethylamine (TEA), copper(I) chloride, diethylamine, formic acid, acetic anhydride, sodium hydrogen carbonate (NaHCO₃), magnesium sulfate, sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), phosphoryl chloride (POCl₃), tetra-*n*-butylammonium bromide (TBAB), nickel(II) chloride hexahydrate (NiCl₂·6H₂O) and nickel(II) chloride (NiCl₂) were purchased from Nacalai Tesque Inc. and used as received. *Trans*-dichlorobis(triethylphosphine) palladium (II) and Iron oxide (II, III), magnetic nanoparticles solution (10 nm avg. part. size, 5 mg/mL in toluene) was purchased from Sigma Aldrich (now Merck). DCM was distilled prior to use. Polystyrene standard was purchased from TOSOH corporation. Poly(3-octylthiophene) was synthesized by Grignard metathesis reaction from dibromo-3-octylthiophene using Ni(dppp)Cl₂.

Instrumentation and method

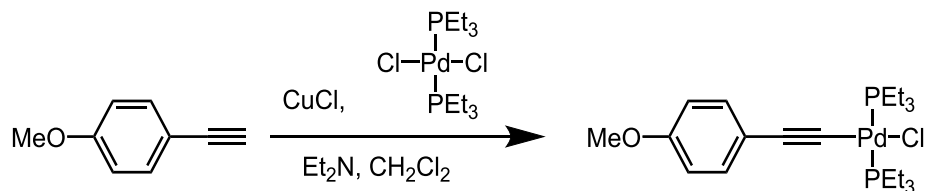
¹H NMR and ¹³C NMR spectra were recorded using a JNM-ECS (JEOL, 400 MHz). Chemical shifts were given in parts per million and coupling constant (*J*) in Hz. Microscopic observations were performed under crossed Nicols using a Nikon Eclipse LV100 polarising optical microscope (POM) equipped with a JHT TH-600PM and a L-600 heating and cooling stage (Linkam). UV-vis absorption spectra were obtained using a JASCO V-630 UV-vis spectrophotometer. CD spectra were obtained using a Jasco J-720 spectrometer. Molecular weights of the polymers were determined by GPC against polystyrene standards by using THF as eluent with 5 mm MIXED-D column (Polymer Laboratories), PU-980 HPLC pump (Jasco), and MD-915 multiwavelength detector (Jasco). FT-IR spectra were recorded using Jasco FT-IR 4600 spectrometer using KBr method. The height profile of C₆₀ spheres and fibres, and the image of PPI smectic ordering was observed using AFM (NanoNavi/S-image with SI-DF20 cantilever). To measure the length of the C₆₀ whiskers and rods, we performed image analysis using ImageJ (obtained from the U.S. National Institutes of Health) on the images obtained from optical microscopy. Scanning electron microscopy images and element mapping were obtained using a JSM-7000F (NIMS, Nanotechnology Platform) with EDX apparatus. For SEM measurement, the sample was coated with Pt (ca. 5 nm). SQUID measurements were carried out using a Quantum Design MPMS-5SPL SQUID magnetometer with a field of 0.1 T in range of 5 – 290 K. ESR measurements were performed at room temperature using a JEOL JES-TE200 ESR spectrometer equipped with a JEOL X-band microwave unit. Synchrotron X-ray diffraction measurement for films was performed on a BL-8B and BL-8C in synchrotron KEK. 1D Out-of-plane 2 θ / θ scan diffraction measurement (wavelength of X-ray: 1.3761Å) was performed using a Rigaku Smartlab equipped with scintillation detector in

Figure 2h. 2D GIXRD measurements (incident angle: $\pm 2.5^\circ$, wavelength: 0.9965 Å) using imaging plate were carried out in Figure 7d, S7, S24, S33-36. The wavelength was calibrated by CeO₂.

Syntheses

Synthesis of Pd complex for living polymerisation of phenylisocyanides

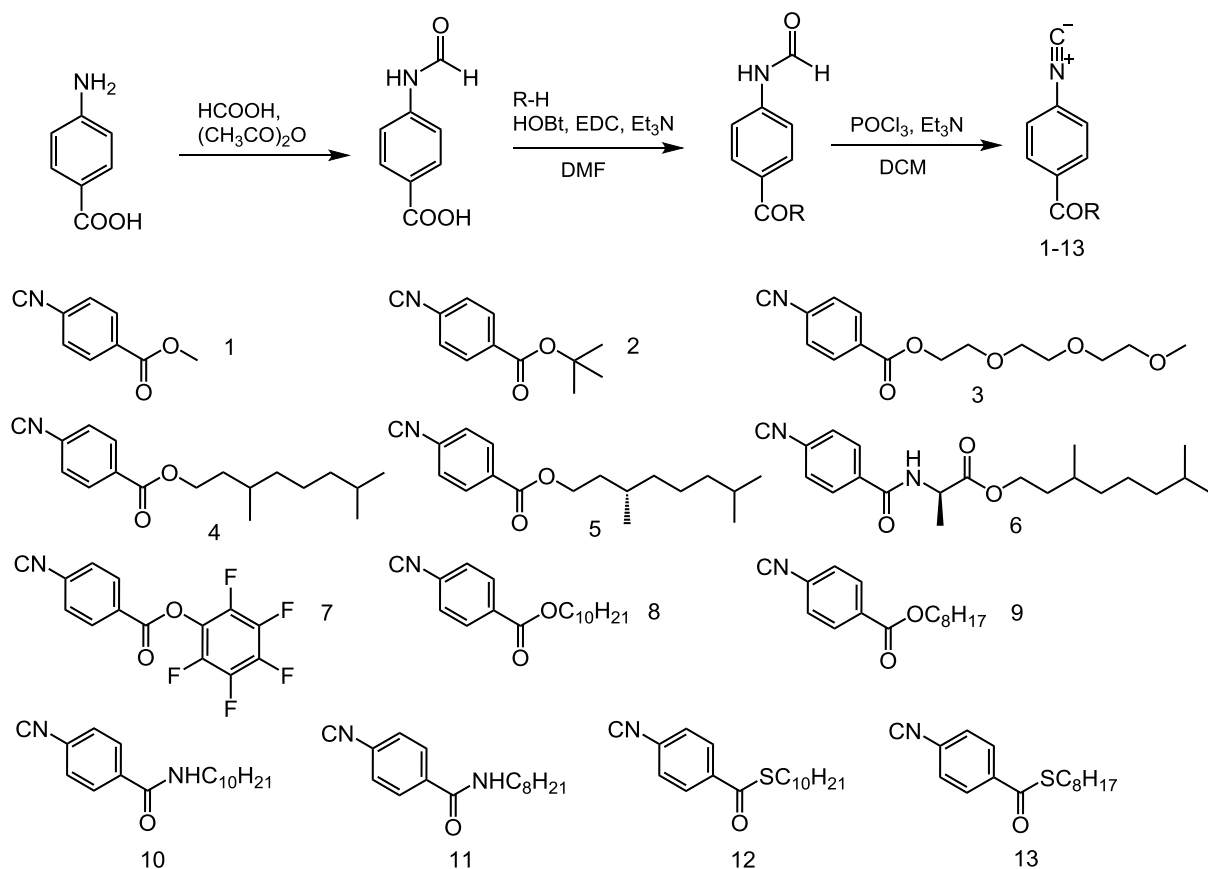
Scheme



4-Methoxy-phenylethynyl Pd complex; This product was synthesized according to the literature¹ and the structure was confirmed by matching its spectroscopic data with corresponding reported data¹. White solid (269 mg, 66%). ¹H NMR (400 MHz, CDCl₃, δ from TMS): δ 7.19 (d, 2H, *J* = 8.8 Hz), 6.78 (d, 2H, *J* = 8.4 Hz), 3.79 (s, 3H), 2.02-1.94 (m, 12H), 1.21 (quint., 18H, *J* = 8.0 Hz).

Synthetic procedure for newly phenylisocyanide monomers

Scheme

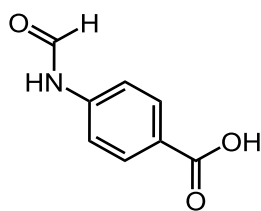


Procedure for formylation reaction

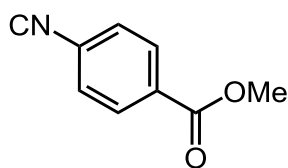
To the oven-dried three neck flask were added 4-aminobenzoic acid (15.00 g, 109 mmol) and formic acid (50 mL). The solution was heated up to 55 °C. Then, acetic anhydride (40 mL) was added dropwise via syringe, and the reaction mixture was stirred for 30 min at 55 °C and for another 3 h at room temperature. The solvent was evaporated under reduced pressure. The obtained solid was suspended in diethylether overnight to remove the residual acid. The suspension was filtered to afford white solid (17.75 g, 98%). This product was used in the subsequent reactions without further purification.

Procedure for condensation and dehydration reactions

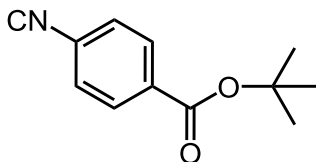
Typical procedure as follows. To the flask were added 4-formamidobenzoic acid (5.01 g, 30.2 mmol) in DMF (50 mL), HOBt·H₂O (4.63 g, 30.2 mmol), EDC·HCl (5.80 g, 30.2 mmol), TEA (4.2 mL, 30.2 mmol), and 3,7-dimethyl-1-octanol (11.51 g, 72.7 mmol). The reaction mixture was stirred at room temperature 17 h. The mixture was extracted with ethylacetate, and washed with Na₂CO₃aq, NaHCO₃aq, water, and brine. The combined organic phase was dried over MgSO₄. The crude product was purified by column chromatography (hexane/ethylacetate = 4/1 - 3/2 (v/v)) and subsequent vacuum drying to afford very viscous colorless oil (7.11 g, 77%). To the oven-dried two neck flask were added (3,7-dimethyloctyl)-4-formamidobenzoate (2.95 g, 6.0 mmol), DCM (20 mL), and TEA (3.4 mL, 15 mmol) under Ar gas atmosphere. The mixture was cooled to 0 °C in the ice bath. Then POCl₃ (0.87 mL, 6.0 mmol) was added dropwise over 10 min. The reaction mixture was stirred at 0 °C for 2.5 h. The reaction was quenched by addition of Na₂CO₃aq at 0 °C and vigorously stirred for 1 h. The mixture was washed with Na₂CO₃aq, NaHCO₃aq, water, and brine three times, respectively. The organic phase was dried over Na₂SO₄. The crude product was purified by column chromatography (hexane/ethylacetate = 4/1 (v/v)) to afford pale yellow-green oil (1.53 g, 55%).



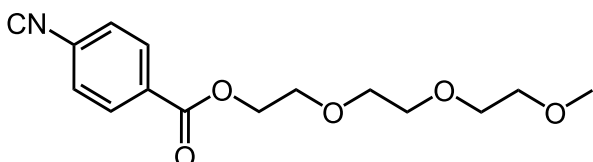
4-Formamidobenzoic acid; White solid (Yield: 98%). This product was synthesized according to the literature² with a little modification. The structure was confirmed by matching its spectroscopic data with corresponding reported data². ¹H NMR (400 MHz, DMSO-d₆, δ from TMS): δ 10.52 (s, 0.9H) 10.44 (d, 0.4H, *J* = 10.4 Hz), 8.96 (d, 0.3H, *J* = 10.8 Hz), 8.34 (d, 0.9H, *J* = 2.0 Hz), 7.92 – 7.87 (2.6H), 7.69 (d, 2H), 7.30 (d, 0.7H, *J* = 8.0 Hz). ¹³C NMR (100 MHz, DMSO-d₆, δ from TMS): δ 160.00, 142.02, 130.82, 130.41, 118.41, 116.26, 99.37.



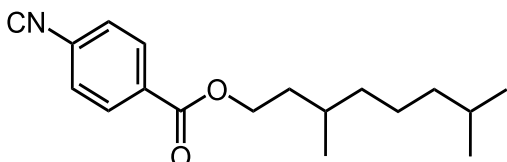
Methyl-4-isocyanobenzoate (1); Yellow solid. The structure was confirmed by matching its spectroscopic data with corresponding reported data³. ¹H NMR (400 MHz, CDCl₃, δ from TMS): δ 8.09 (d, 2H, *J* = 8.8 Hz), 7.45 (d, 2H, *J* = 8.8 Hz), 3.94 (s, 3H).



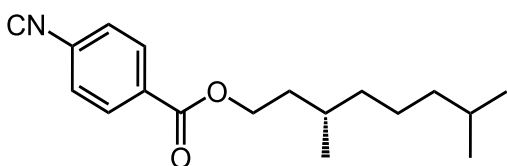
tert-Butyl-4-isocyanobenzoate (2); White crystal (Yield: 36% in 2 steps). This product was synthesized from tert-butyl-4-aminobenzoate. The structure was confirmed by matching its spectroscopic data with corresponding reported data⁴. ¹H NMR (400 MHz, CDCl₃, δ from TMS): δ 8.02 (dd, 2H, *J* = 6.8 Hz), 7.42 (dd, 2H, *J* = 6.8 Hz), 1.60 (s, 9H).



(Triethylene glycol monomethyl)-4-isocyanobenzoate (3); Yellow liquid (Yield: 9% in 2 steps). The structure was confirmed by matching its spectroscopic data with corresponding reported data⁵. ¹H NMR (400 MHz, CDCl₃, δ from TMS): δ 8.11 (dd, 2H, *J* = 6.8 Hz), 7.45 (d, 2H, *J* = 8.8 Hz), 4.49 (t, 2H, *J* = 4.8 Hz), 3.84 (t, 2H, *J* = 4.8 Hz), 3.73-3.64 (m, 6H), 3.55-3.53 (m, 2H), 3.37 (s, 3H).

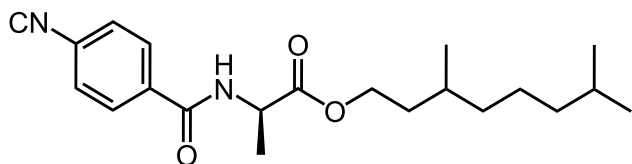


(3,7-Dimethyloctyl)-4-isocyanobenzoate (4); Yellow-green liquid (Yield: 42% in 2 steps). ¹H NMR (400 MHz, CDCl₃, δ from TMS): δ 8.08 (dd, 2H, *J* = 6.8 Hz), 7.44 (dd, 2H, *J* = 6.8 Hz), 4.40-4.36 (m, 2H), 1.82-1.80 (m, 1H), 1.62-1.51 (m, 3H), 1.35-1.31 (m, 3H), 1.19-1.14 (m, 3H), 0.96 (d, 3H, *J* = 6.4 Hz), 0.87 (d, 6H, *J* = 6.4 Hz). ¹³C NMR (100 MHz, CDCl₃, δ from TMS): δ 166.96, 164.94, 131.22, 130.70, 126.32, 64.12, 39.08, 37.01, 35.38, 29.86, 27.85, 27.84, 24.52, 22.60, 22.50, 19.51. FT-IR (KBr, cm⁻¹): 2121 (ν_{C=N}), 1725 (ν_{C=O}).

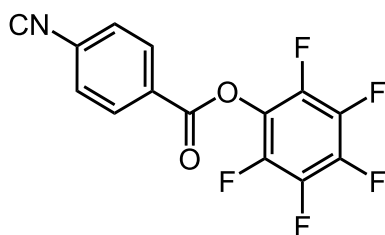


((3S)-3,7-Dimethyloctyl)-4-isocyanobenzoate (5); Yellow-green liquid (Yield: 42% in 2 steps). ¹H NMR (400 MHz, CDCl₃, δ from TMS): δ 8.08 (dt, 2H, *J* = 8.4 Hz), 7.44 (dd, 2H, *J* = 6.8 Hz), 4.40-4.35 (m, 2H), 1.80 (m, 1H),

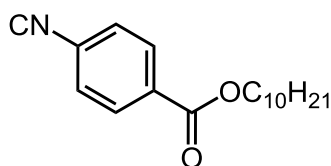
1.61-1.49 (m, 3H), 1.35-1.25 (m, 3H), 1.19-1.12 (m, 3H), 0.96 (d, 3H, $J = 6.8$ Hz), 0.87 (d, 6H, $J = 6.4$ Hz). ^{13}C NMR (100 MHz, CDCl_3 , δ from TMS): δ 168.96, 165.04, 131.31, 130.78, 126.41, 64.21, 39.16, 37.09, 35.46, 29.95, 27.93, 24.60, 22.65, 22.57, 19.57.



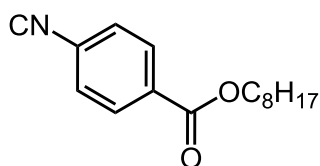
(L-alanine-based-3,7-dimethyloctylester)-4-isocyanobenzamine (6); Yellow solid (Yield: 25% in 2 steps). ^1H NMR (400 MHz, CDCl_3 , δ from TMS): δ 7.85 (d, 2H, $J = 8.8$ Hz), 7.45 (d, 2H, $J = 8.8$ Hz), 6.87 (d (broad), 1H, $J = 7.2$ Hz), 7.85 (quint., 1H, $J = 7.2$ Hz), 4.26-4.21 (m, 2H), 1.76-1.70 (m, 2H), 1.56-1.46 (m, 6H), 1.32-1.22 (m, 3H), 1.18-1.11 (m, 3H), 0.91 (d, 3H, $J = 6.0$ Hz), 0.87 (d, 6H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, CDCl_3 , δ from TMS): δ 204.97, 173.13, 134.69, 128.34, 126.58, 64.41, 54.63, 48.72, 48.70, 39.11, 37.06, 36.99, 35.35, 30.26, 29.75, 29.72, 27.90, 24.58, 22.64, 22.55, 19.40, 18.55.



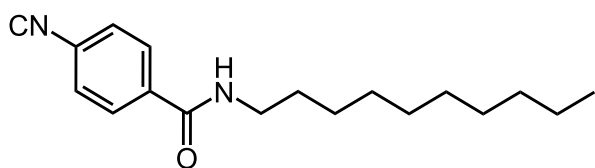
Pentafluorophenyl-4-isocyanobenzoate (7); Yellow solid (Yield: 41% in 2 steps). The structure was confirmed by matching its spectroscopic data with corresponding reported data⁶. ^1H NMR (400 MHz, CDCl_3 , δ from TMS): δ 8.26 (d, 2H, $J = 8.8$ Hz), 7.57 (d, 2H, $J = 8.8$ Hz).



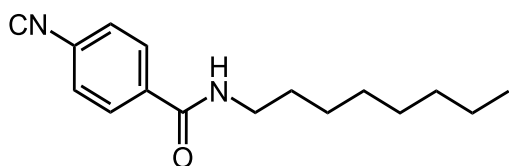
Decyl-4-isocyanobenzoate (8); Pale-yellow solid (Yield: 17% in 2 steps). The structure was confirmed by matching its spectroscopic data with corresponding reported data⁷. ^1H NMR (400 MHz, CDCl_3 , δ from TMS): δ 8.08 (dt, 2H), 7.45 (dt, 2H), 4.33 (t, 2H, $J = 6.4$ Hz), 1.77 (quint., 2H, $J = 7.2$ Hz), 1.45-1.28 (m, 14H), 0.88 (t, 3H, $J = 6.8$ Hz).



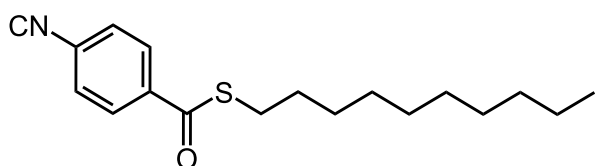
Octyl-4-isocyanobenzoate (9); This product was synthesized in our previous report⁸, and the same sample was used in this study.



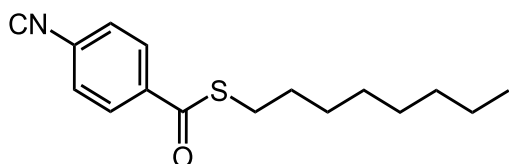
***N*-decyl-4-isocyanobenzamine (10)**; White crystal (Yield: 10% in 2 steps). ^1H NMR (400 MHz, CDCl_3 , δ from TMS): δ 7.80 (d, 2H, $J = 8.0$ Hz), 7.44 (d, 2H, $J = 8.0$ Hz), 6.18 (broad, 1H), 3.44 (quart., 2H, $J = 6.8$ Hz), 1.61 (quint., 2H, $J = 7.6$ Hz), 1.35-1.26 (m, 14H), 0.88 (t, 3H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3 , δ from TMS): δ 216.38, 172.74, 165.70, 135.64, 128.13, 126.57, 40.30, 31.84, 29.54, 29.50, 29.26, 26.95, 22.64, 14.09.



***N*-octyl-4-isocyanobenzamine (11)**; White crystal (Yield: 8% in 2 steps). ^1H NMR (400 MHz, CDCl_3 , δ from TMS): δ 7.80 (d, 2H, $J = 8.8$ Hz), 7.45 (d, 2H, $J = 8.8$ Hz), 6.08 (broad, 1H), 3.46 (quint., 2H, $J = 6.0$ Hz), 1.62 (quint., 2H, $J = 6.8$ Hz), 1.38-1.27 (m, 10H), 0.88 (t, 3H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3 , δ from TMS): δ 209.37, 186.68, 165.70, 135.66, 128.12, 126.62, 40.32, 31.77, 29.57, 29.24, 29.18, 26.96, 22.62, 14.08.



4-Isocyanobenzoic acid decyl thioester (12); Yellow solid (Yield: 18% in 2 steps). ^1H NMR (400 MHz, CDCl_3 , δ from TMS): δ 8.00 (dt, 2H), 7.46 (dt, 2H), 3.09 (t, 2H, $J = 7.2$ Hz), 1.67 (quint., 2H, $J = 7.6$ Hz), 1.46 - 1.38 (m, 2H), 1.34 - 1.26 (m, 12H), 0.88 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, CDCl_3 , δ from TMS): δ 190.58, 182.03, 162.88, 137.58, 128.38, 126.65, 93.07, 84.40, 31.86, 29.52, 29.46, 29.40, 29.36, 29.28, 29.11, 28.89, 22.66, 14.11, 8.13. FT-IR (KBr, cm^{-1}): 2138 and 2123 ($\nu_{\text{C}=\text{N}}$), 1658 ($\nu_{\text{C}=\text{O}}$).



4-Isocyanobenzoic acid octyl thioester (13); Yellow solid (Yield: 18% in 2 steps). This compound was synthesized by the same procedure as compound 12. ^1H NMR (400 MHz, CDCl_3 , δ from TMS): δ 8.00 (dt, 2H, $J = 8.4$ Hz), 7.45 (dt, 2H, $J = 8.8$ Hz), 3.09 (t, 2H, $J = 7.6$ Hz), 1.68 (quint., 2H, $J = 7.2$ Hz), 1.58-1.39 (m, 2H), 1.36-1.28 (m, 8H), 0.88 (t, 3H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3 , δ from TMS): δ 209.66, 190.53, 137.58, 135.11, 128.36, 126.63, 31.75, 29.38, 29.35, 29.11, 29.05, 28.87, 22.60, 14.05.

Polymerisation

Pd complex initiated living polymerisation for controlled molecular weight, narrowly dispersed poly8 (entry 15-27)

Into an oven-dried three neck flask was added decyl-4-isocyanobenzoate (288 mg, 1.0 mmol) in THF (9.5 mL) under Ar gas atmosphere. The solution was heated up to 55 °C, and then 4-methoxy-phenylethynyl Pd complex (2.65 mg, 0.0052 mmol) in THF (0.5 mL) was added to the solution to initiate the living polymerisation. The reaction mixture was stirred at 55 °C. During the polymerisation, the aliquots (0.1-0.5 mL) were taken from the reaction mixture at different time periods (20 min, 40 min, 1h, 1.5 h, 2 h, 2.5 h, 4 h, 5.5 h, 6.5 h, 7.5 h, 8 h, 9 h, 9.5 h) to monitor the progress of the living polymerisation (Figure S1). Each aliquot was quenched with methanol to yield yellow precipitates. The precipitated polymers were collected by centrifugation (15000 rpm, 20 min) and washed with methanol 3 times. The collected polymers were dried under vacuum to afford controlled molecular weight, narrowly dispersed **poly8**.

NiCl₂·6H₂O catalyzed polymerisation of isocyanide for PPIs

Typical procedure is as follows: Into an oven-dried Schlenk flask was added isocyanide monomer solution in THF or in DCM 3 mL (0.1 M) under Ar gas atmosphere. Then, NiCl₂·6H₂O (0.02 equiv.) in ethanol (0.01 M) was added. The reaction mixture was stirred at room temperature for 1-3 days, where the solution turned into viscous orange from pale yellow. The reaction was quenched with methanol to yield yellow fibre-like precipitates. The precipitated PPIs were collected by centrifugation (3000 rpm, 10 min) and washed with methanol 3 times. The collected PPIs were dried under vacuum.

NiCl₂ catalyzed polymerisation of isocyanide for PPIs

Typical procedure is as follows: Into an oven-dried Schlenk flask was added isocyanide monomer solution in DCM 3 mL (0.1 M) under Ar gas atmosphere. Then, NiCl₂ (0.02 equiv.) solid was added and dispersed. The reaction mixture was stirred at room temperature for 3 days, where the solution turned into viscous orange from pale yellow. The reaction was quenched with methanol to yield yellow fibre-like precipitates. The precipitated PPIs were collected by centrifugation (3000 rpm, 10 min) and washed with methanol 3 times. The collected PPIs were dried under vacuum.

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Table S1. GPC results and lyotropic liquid crystallinity for PPIs.

Entry	Polymer	Initiator	Solvent	M_n^a (kDa)	M_w/M_n^a	Yield ^c	LC ^e
1	Poly1	NiCl ₂ ·6H ₂ O	THF	176.8 ^b	2.96 ^b	>99%	++
2	Poly2	NiCl ₂ ·6H ₂ O	THF	86.6	2.25	39%	+
3	Poly3	NiCl ₂ ·6H ₂ O	THF	422.3	2.19	84%	++
4	Poly4	NiCl ₂ ·6H ₂ O	THF	293.4	1.76	78%	++
5	Poly5	NiCl ₂ ·6H ₂ O	THF	191.9	2.21	91%	++
6	Poly6	NiCl ₂ ·6H ₂ O	THF	418.9	1.70	>99%	++
7	Poly7	NiCl ₂	DCM	471.0	2.28	94%	N/A ^f
8	Poly8	NiCl ₂ ·6H ₂ O	DCM	57.3	1.41	>99%	++
9	Poly8	NiCl ₂	DCM	239.6	2.73	>99%	++
10	Poly9	NiCl ₂	DCM	55.2	3.08	88%	++
11	Poly10	NiCl ₂ ·6H ₂ O	THF	258.4	1.75	85%	++
12	Poly11	NiCl ₂ ·6H ₂ O	THF	178.9	1.93	89%	++
13	Poly12	NiCl ₂ ·6H ₂ O	THF	69.3	2.92	92%	++
14	Poly13	NiCl ₂ ·6H ₂ O	THF	93.3	1.71	81%	++
15	Poly8	Pd complex	THF	3.6	1.02	- ^d	-
16	Poly8	Pd complex	THF	4.7	1.07	- ^d	-
17	Poly8	Pd complex	THF	6.2	1.08	- ^d	-
18	Poly8	Pd complex	THF	8.0	1.10	- ^d	+
19	Poly8	Pd complex	THF	9.7	1.12	- ^d	+
20	Poly8	Pd complex	THF	11.3	1.12	- ^d	+
21	Poly8	Pd complex	THF	17.5	1.13	- ^d	+
22	Poly8	Pd complex	THF	23.4	1.12	- ^d	++
23	Poly8	Pd complex	THF	26.2	1.12	- ^d	++
24	Poly8	Pd complex	THF	28.1	1.11	- ^d	++
25	Poly8	Pd complex	THF	29.4	1.10	- ^d	++
26	Poly8	Pd complex	THF	29.9	1.10	- ^d	++
27	Poly8	Pd complex	THF	30.4	1.10	- ^d	++

a. Molecular weight and molecular distribution were estimated by GPC analysis calibrated by PS standard (eluent: THF at rt for **poly1, 4, 5, 7, 8, 9, 12, 13** or THF with 0.1wt% TBAB at rt for **poly2, 3, 6, 10, 11**). b. M_n and M_w/M_n of **poly1** was estimated from GPC with CHCl₃ eluent due to the poor solubility to THF. c. isolated yield. d. the yields could not be determined precisely because they were aliquots (taken at different time periods) from the same reaction mixture. e. lyotropic liquid crystallinity (LC) was evaluated by polarising optical microscopy for drop-cast **PPI** films (see Figure S4, S5). LC was evaluated at three levels: “- (No)”, “+ (a little)”, and “++ (Yes)”. f. not applicable due to the poor film formation ability of **poly7**. THF: tetrahydrofuran, DCM: dichloromethane, Pd complex: 4-methoxy-phenylethynyl Pd complex.

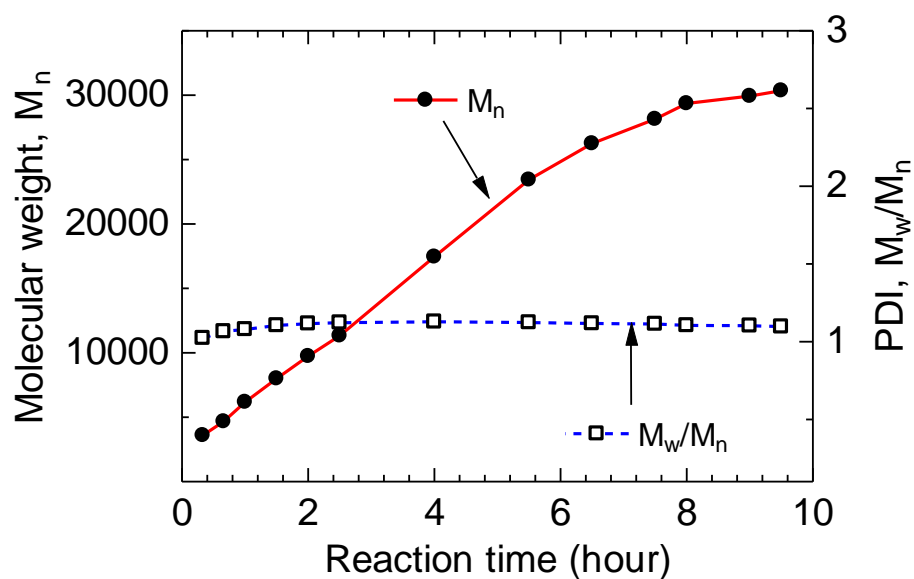


Figure S1. GPC results for a series of **poly8** (entry 15-27) prepared from living polymerisation using Pd complex: time-dependent molecular weight and polydispersity monitoring experiments.

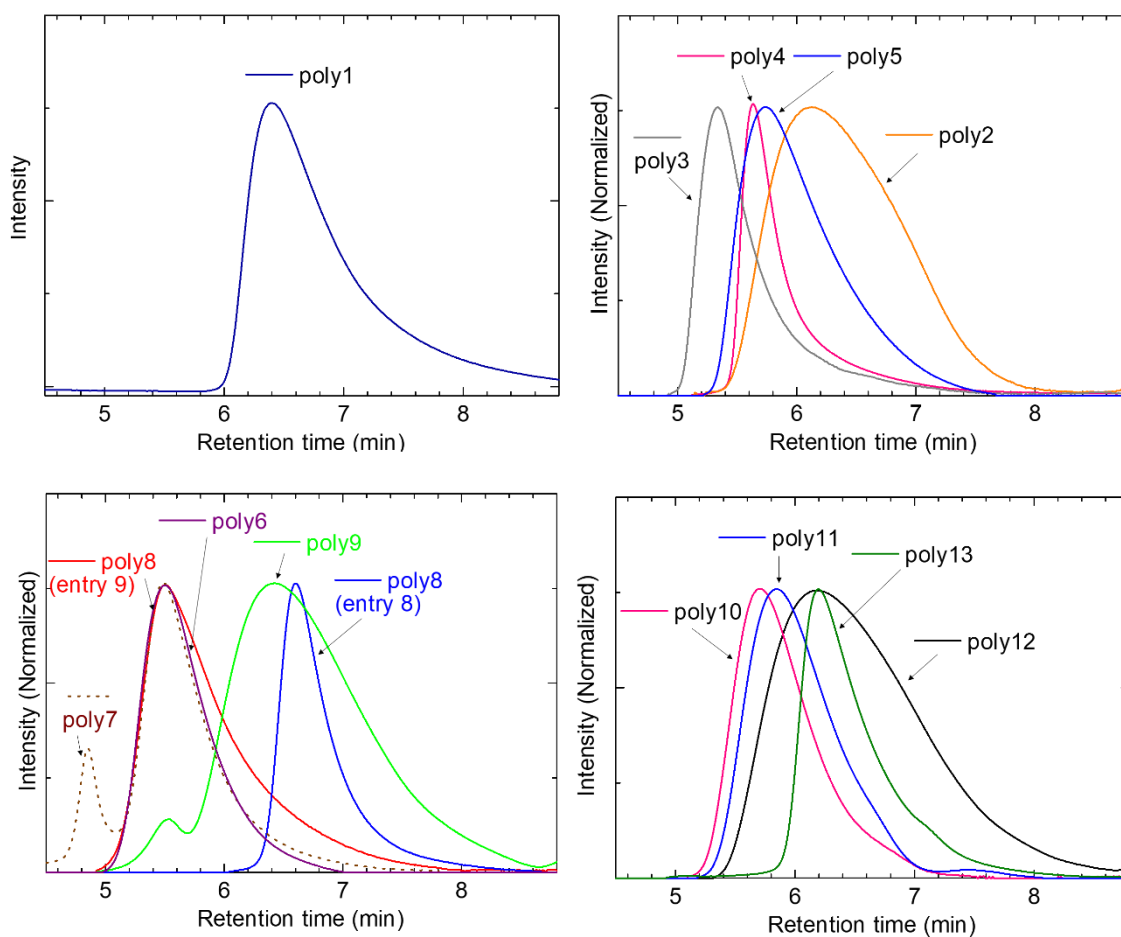


Figure S2. GPC results for **poly1** (CHCl_3 eluent) and **poly2-13** (THF eluent) prepared from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or NiCl_2 .

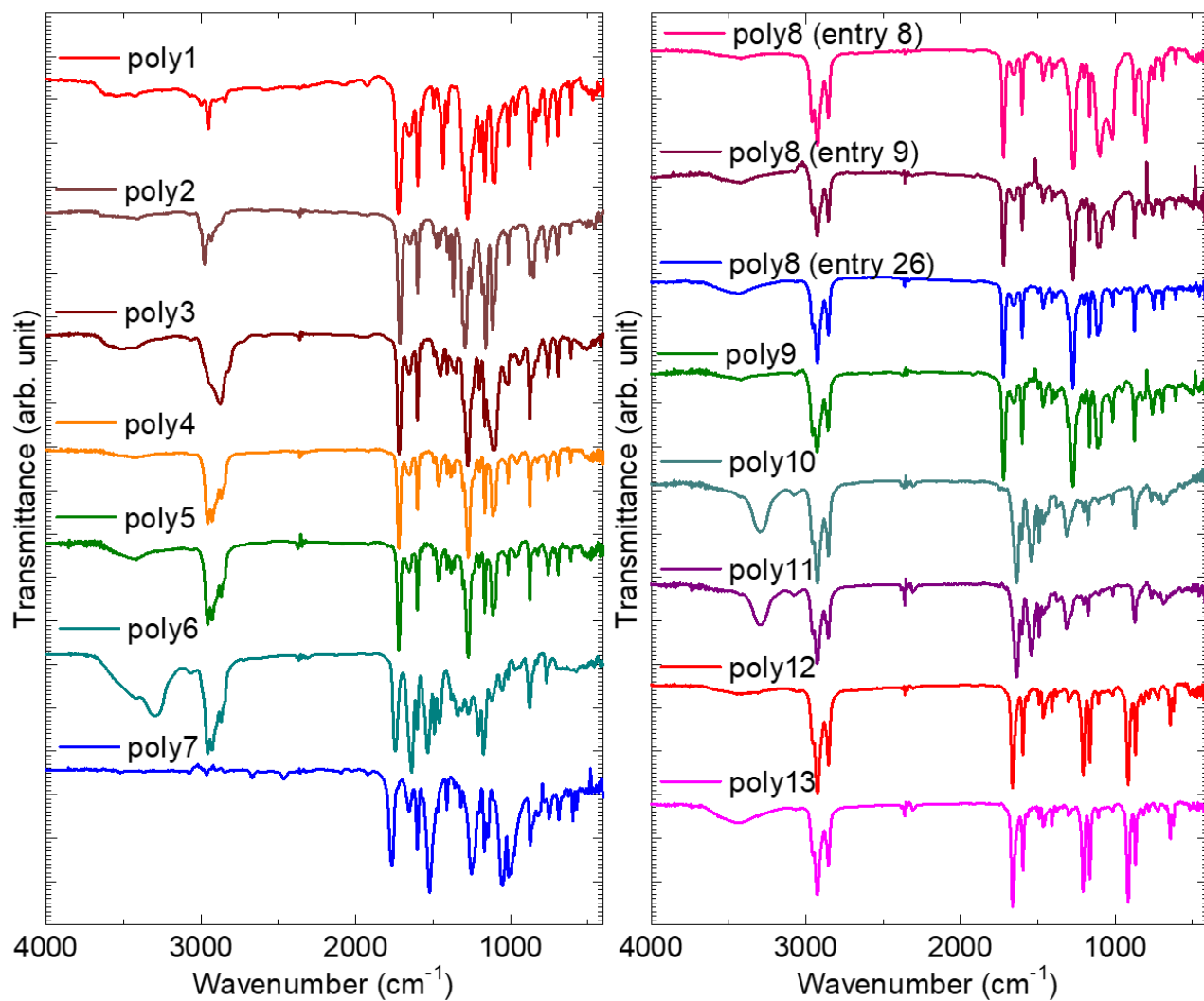


Figure S3. FT-IR spectra of **poly1-7**, **poly8 (entry 8)** (prepared by NiCl₂·6H₂O), **entry 9** (prepared by NiCl₂), **entry 26** (prepared by Pd complex, M_n = 29.9 (kDa), M_w/M_n = 1.10), and **poly9-13**.

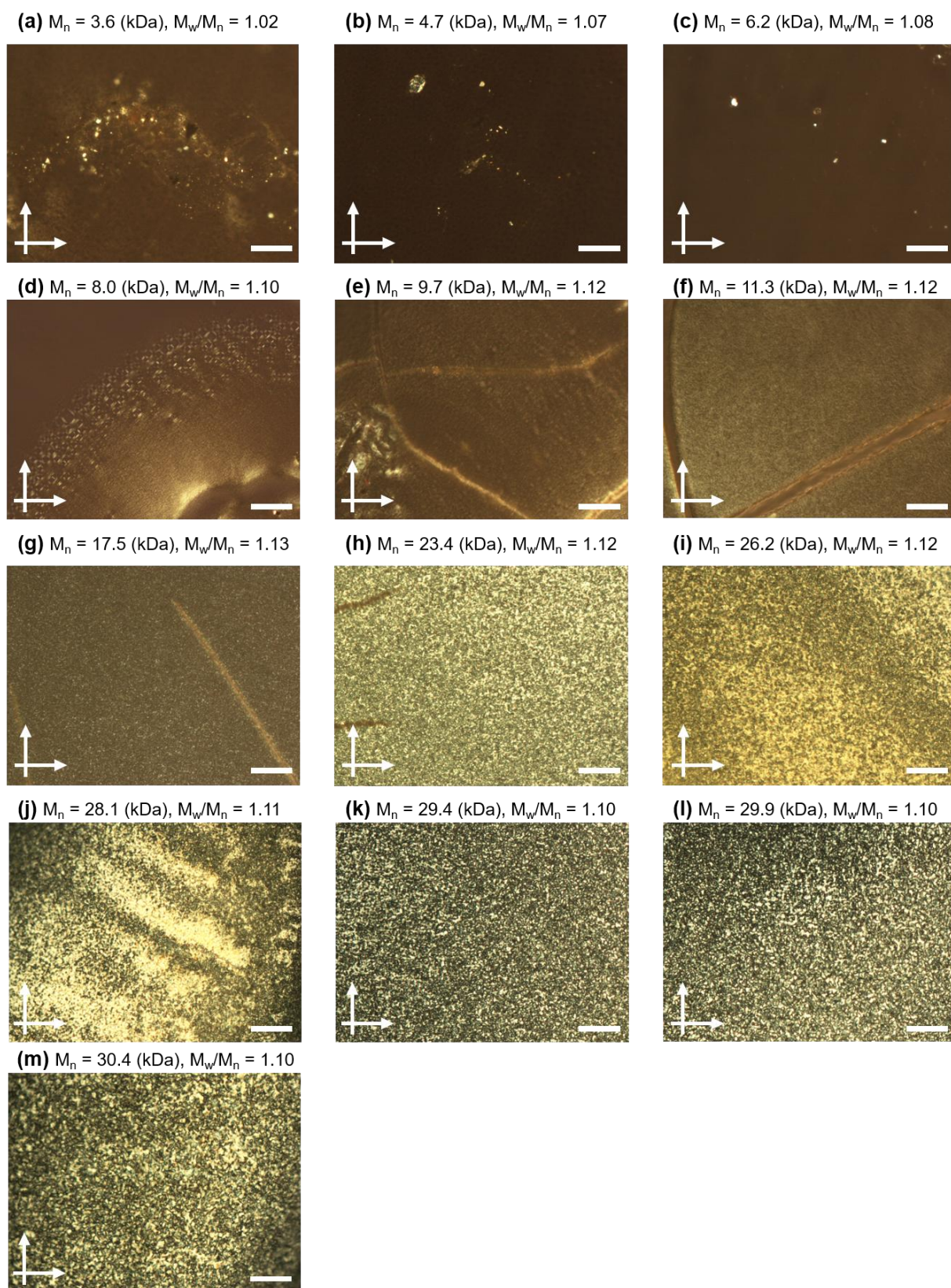


Figure S4. POM images of well-defined, controlled molecular weight, narrowly dispersed **poly8** (entry 15-27) with different molecular weight ($M_n = 3.6 - 30.4$ (kDa), $M_w/M_n < 1.13$) films without fullerene C_{60} prepared from the corresponding toluene solution. The films were observed without annealing treatment. Scale bars, 20 μm .

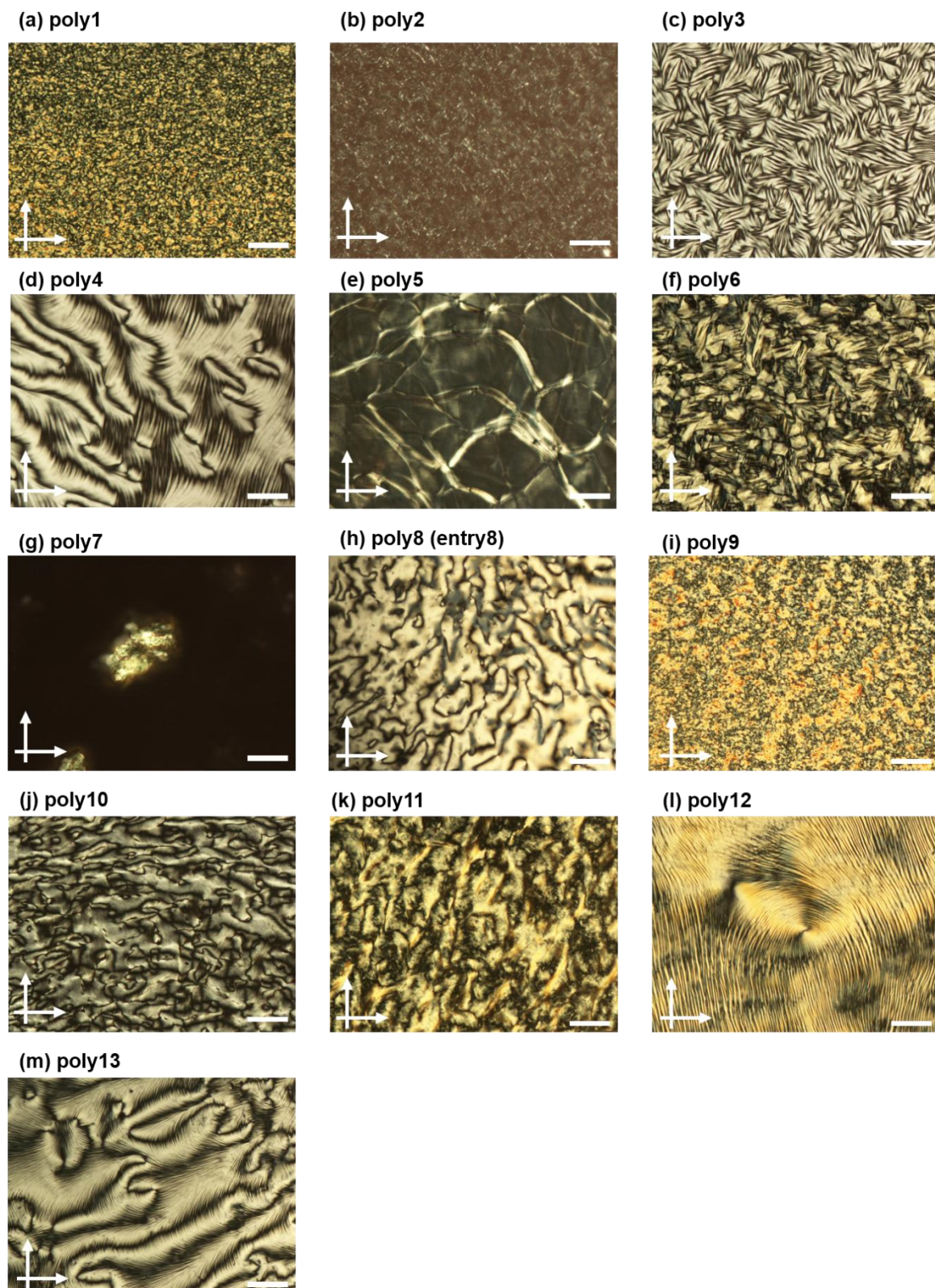


Figure S5. POM images of **PPI** films without fullerene C_{60} prepared from the corresponding toluene solution (for **poly1,2,3,5,6**) or 1,1,2,2-tetrachloroethane (for **poly4**). The films were observed after THF vapor annealing treatment. **Poly7** did not form uniform film but particles that exhibits birefringence. Scale bars, 20 μm .

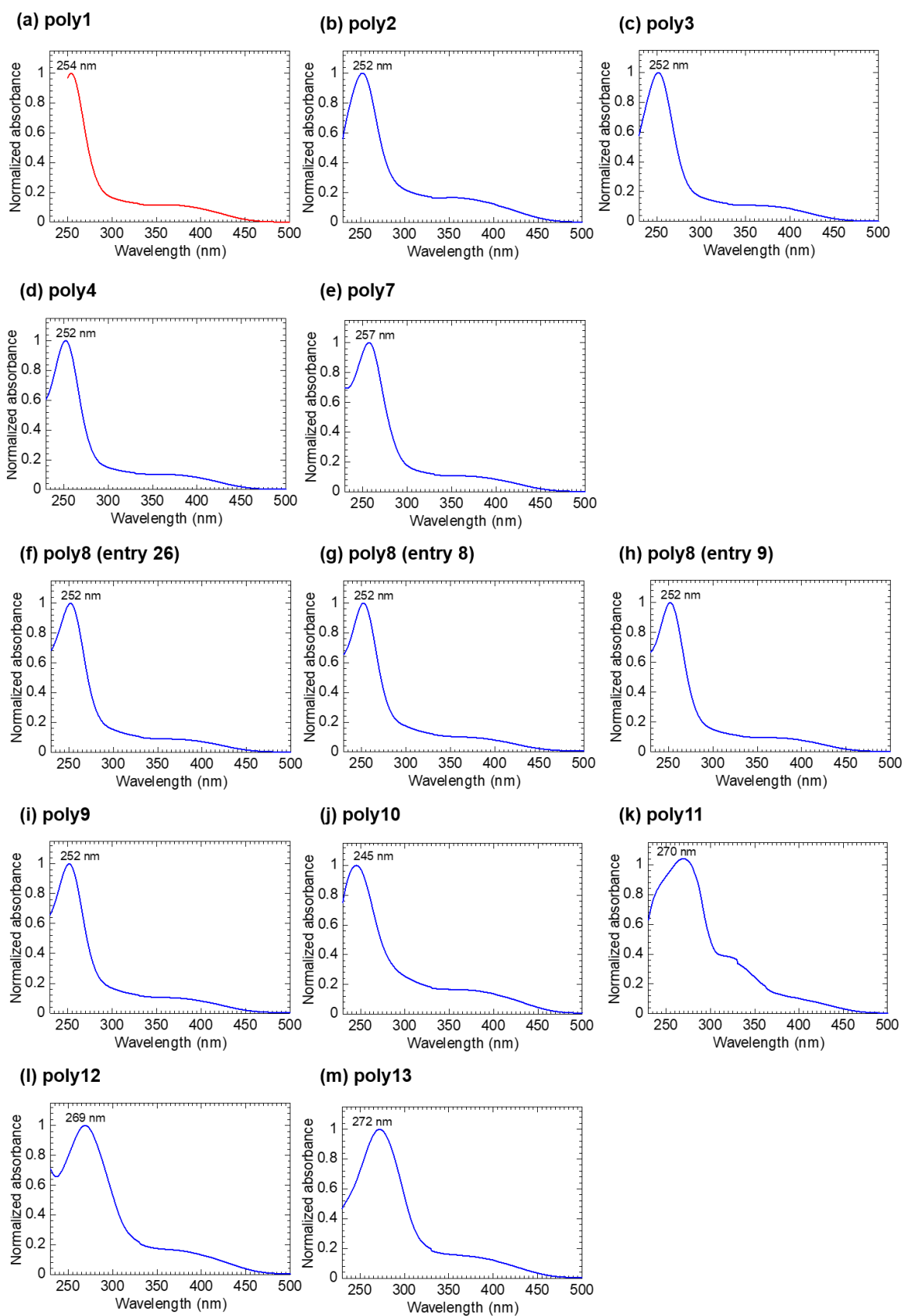


Figure S6. Absorption spectra of PPIs in THF solution (for **poly1-4, 7-13**) or in chloroform (for **poly1**) (0.02 mg/mL). For **poly5, 6**, see Figure S8.

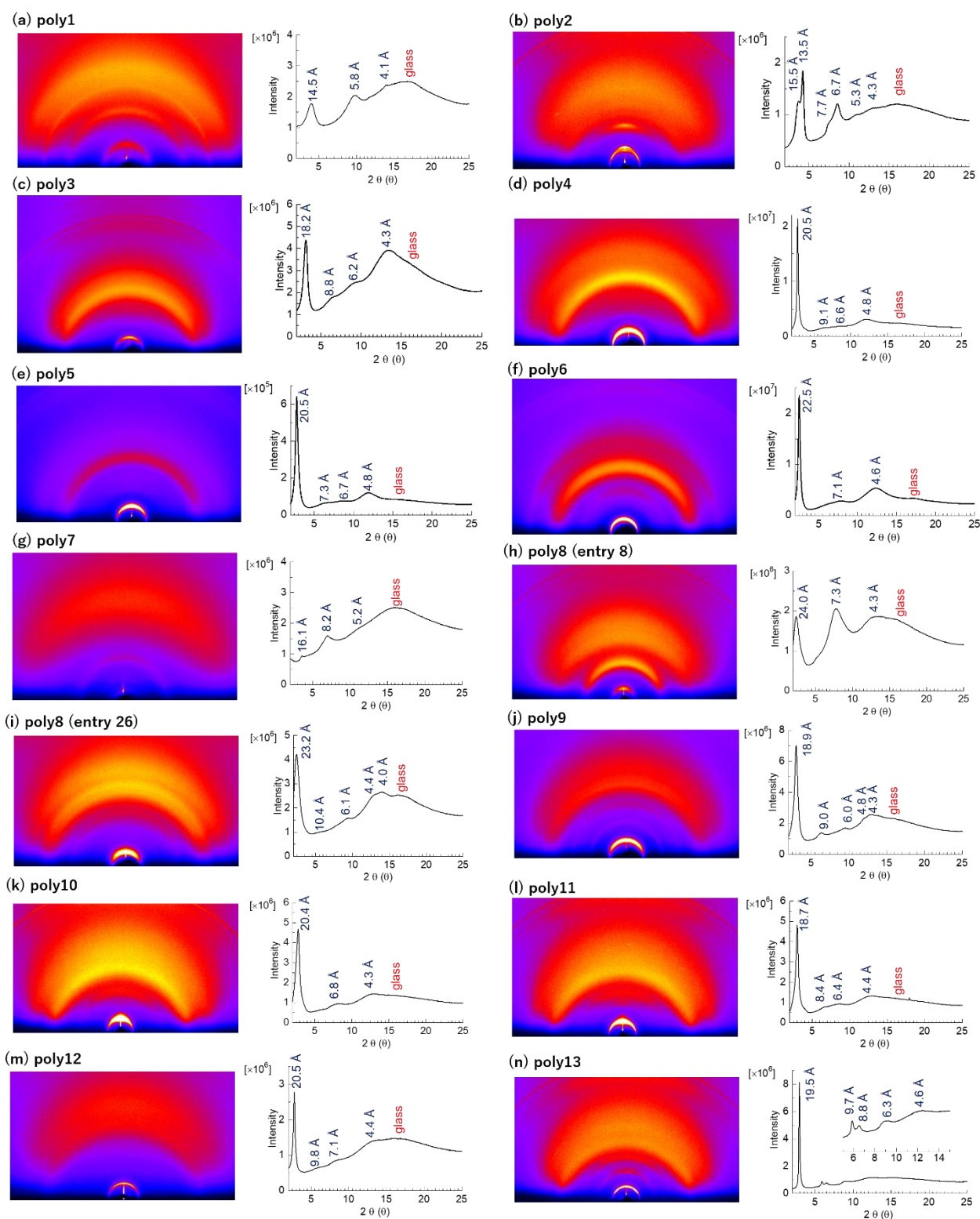


Figure S7. GIXRD profiles for the drop-cast **PPI** films (**poly1,2,3,4,5,6**). **Poly1,2,3,5,6** films were prepared from the corresponding THF solutions, while **poly4** film was prepared from the corresponding chloroform solution. **poly1** was synthesized by Pd complex ($M_n = 29.9$ (kDa), $M_w/M_n = 1.10$). The broad halo at $2\theta \sim 16^\circ$ is due to the amorphous diffraction of the glass substrate. The primary peaks are derived from the interchain packing of **PPIs**.

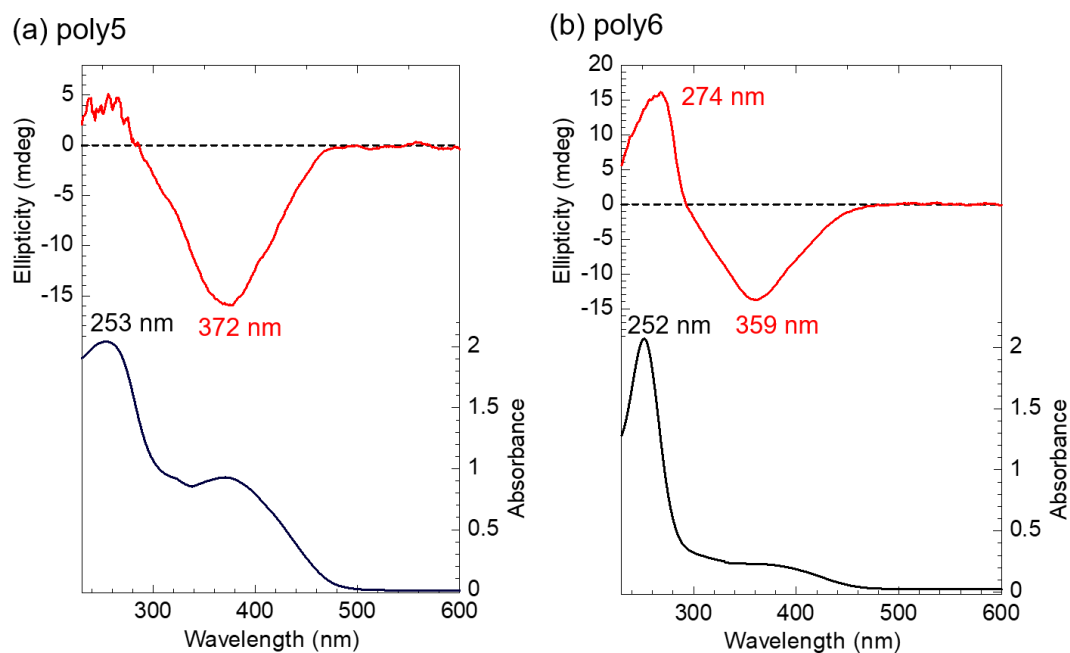


Figure S8. UV-vis absorption and CD spectra for (a) **poly5** and (b) **poly6** in THF solution (0.2 mg/mL)

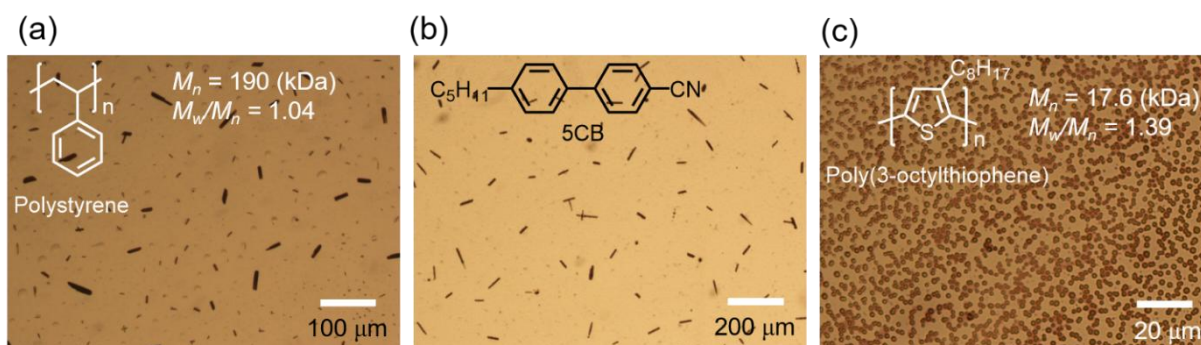


Figure S9. Optical microscopy images of C_{60} assemblies prepared from C_{60} in toluene solution (0.5 mg/mL) with the additives such as (a) polystyrene (PS), (b) 4-cyano-4'-pentylbiphenyl (5CB), and (c) poly(3-octylthiophene) (P3OT), respectively.

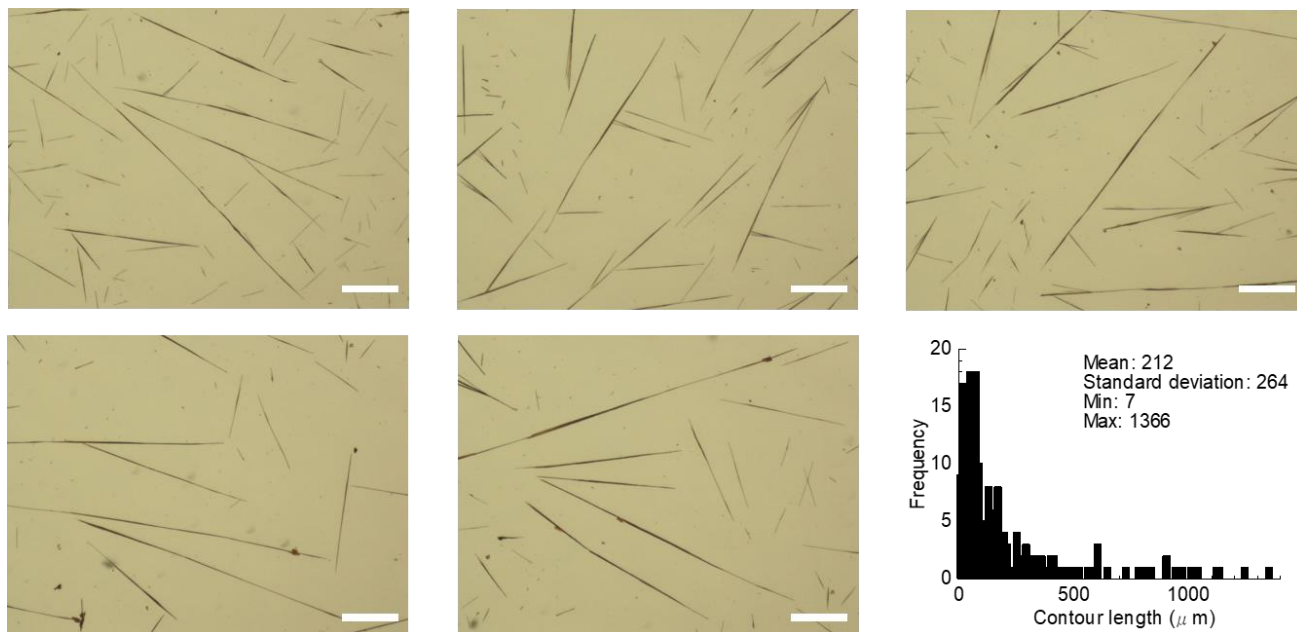


Figure S10. Optical microscopy images of the C_{60} /poly8 composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of poly8 ($M_n = 3.6$ kDa, $M_w/M_n = 1.02$). Scale bars, 200 μm , $N = 203$.

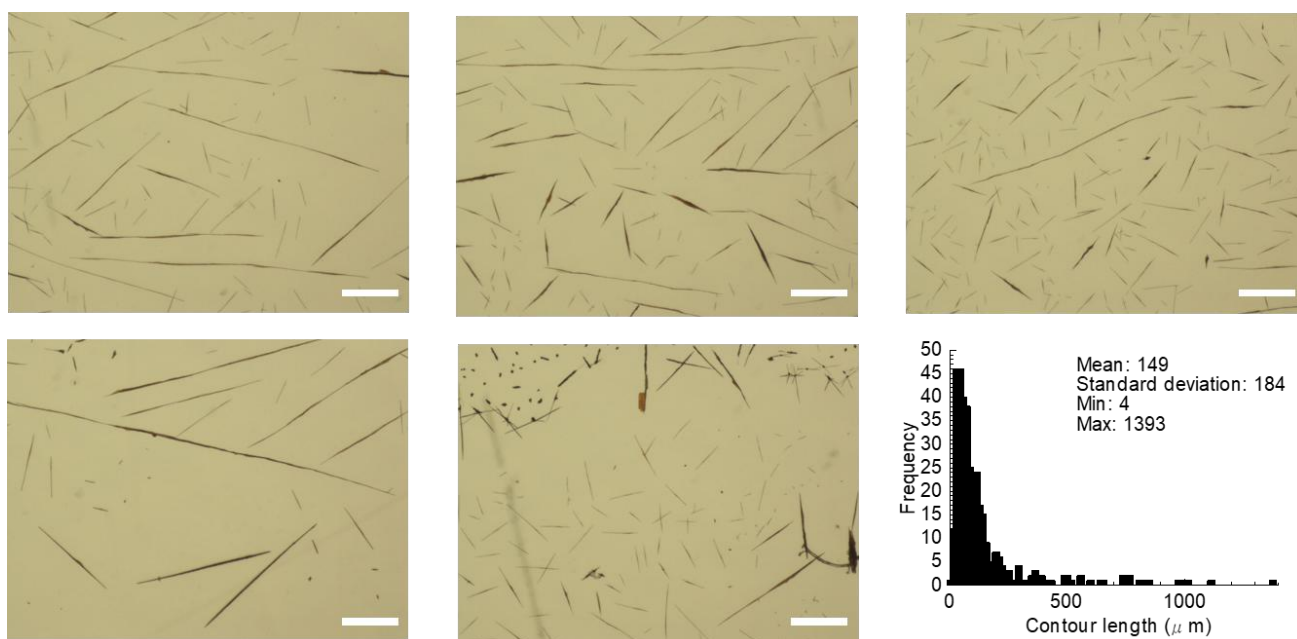


Figure S118. Optical microscopy images of the C_{60} /poly8 composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of poly8 ($M_n = 4.7$ kDa, $M_w/M_n = 1.07$). Scale bars, 200 μm , $N = 370$.

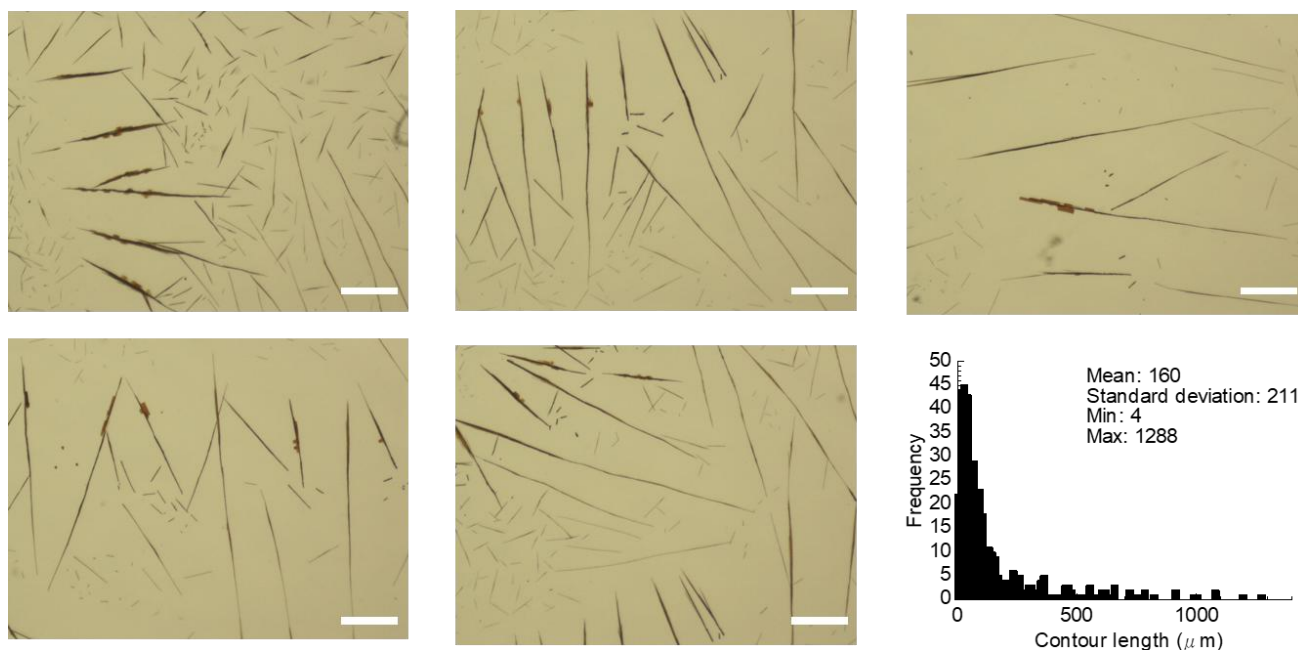


Figure S12. Optical microscopy images of the C_{60} / **poly8** composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of **poly8** ($M_n = 6.2$ kDa, $M_w/M_n = 1.08$). Scale bars, 200 μm , $N = 407$.

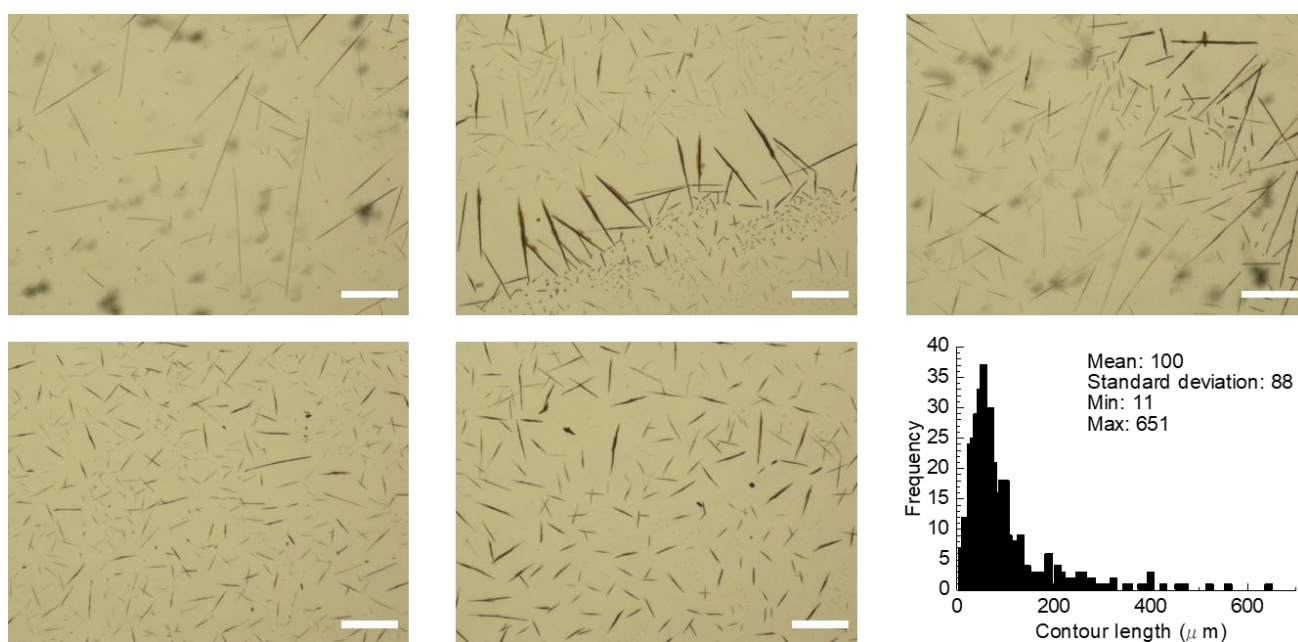


Figure S13. Optical microscopy images of the C_{60} / **poly8** composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of **poly8** ($M_n = 8.0$ kDa, $M_w/M_n = 1.10$). Scale bars, 200 μm , $N = 436$.

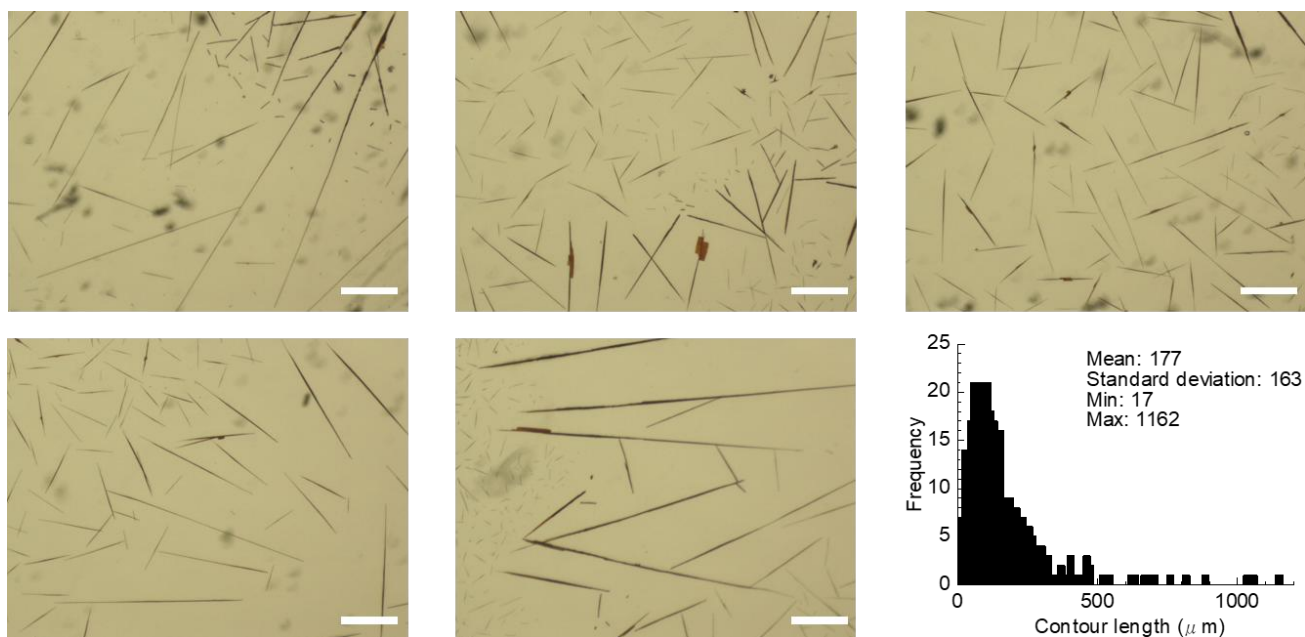


Figure S14. Optical microscopy images of the C_{60} /poly8 composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of poly8 ($M_n = 9.7$ kDa, $M_w/M_n = 1.12$). Scale bars, 200 μm , $N = 323$.

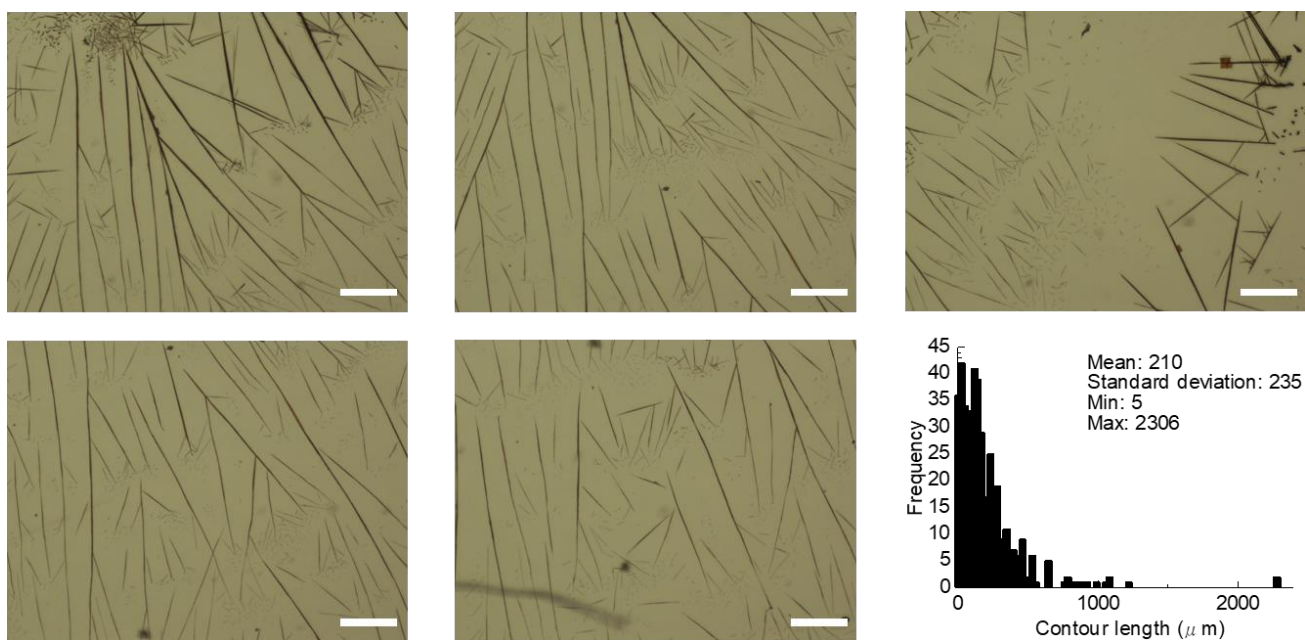


Figure S15. Optical microscopy images of the C_{60} /poly8 composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of poly8 ($M_n = 11.3$ kDa, $M_w/M_n = 1.12$). Scale bars, 200 μm , $N = 448$.

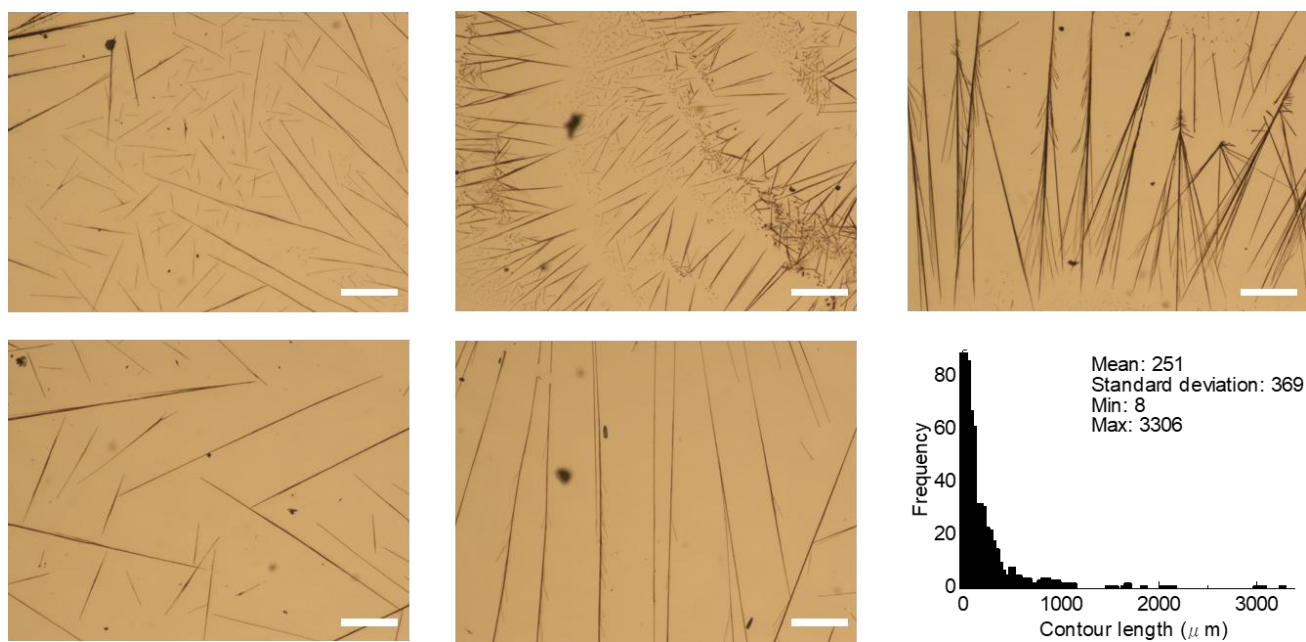


Figure S16. Optical microscopy images of the C_{60} /poly8 composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of poly8 ($M_n = 17.5$ kDa, $M_w/M_n = 1.13$). Scale bars, 200 μm , $N = 569$.

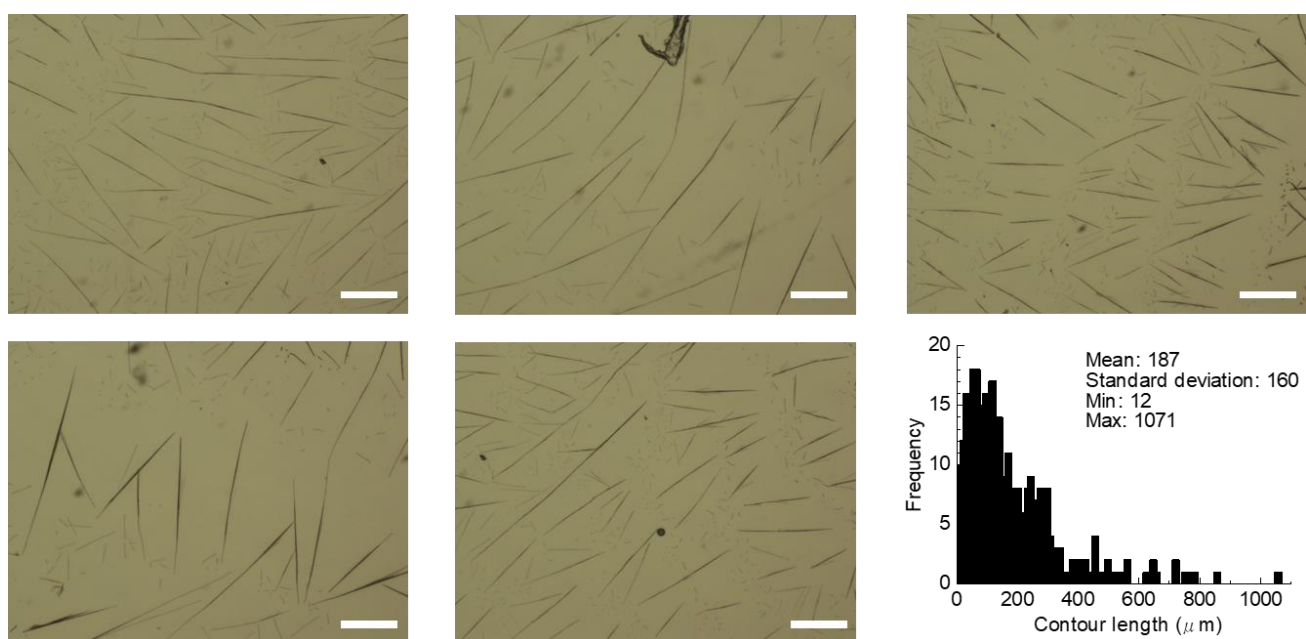


Figure S17. Optical microscopy images of the C_{60} /poly8 composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of poly8 ($M_n = 23.4$ kDa, $M_w/M_n = 1.12$). Scale bars, 200 μm , $N = 341$.

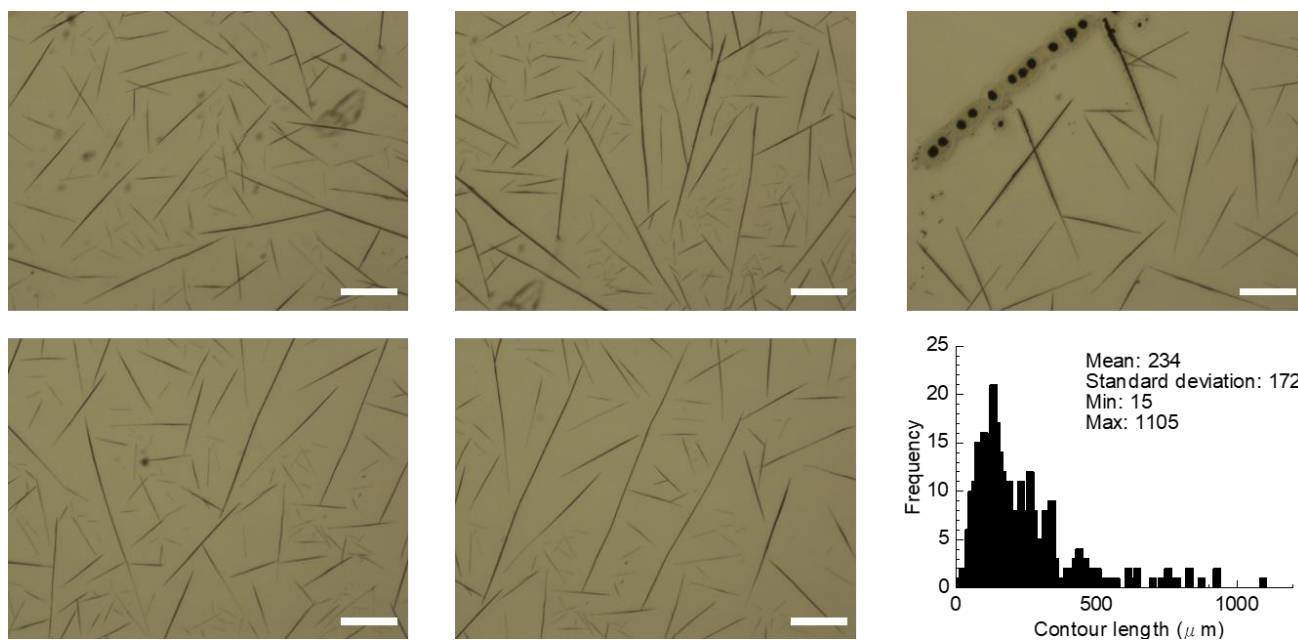


Figure S18. Optical microscopy images of the C_{60} /poly8 composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of poly8 ($M_n = 26.2$ kDa, $M_w/M_n = 1.12$). Scale bars, 200 μm , $N = 342$.

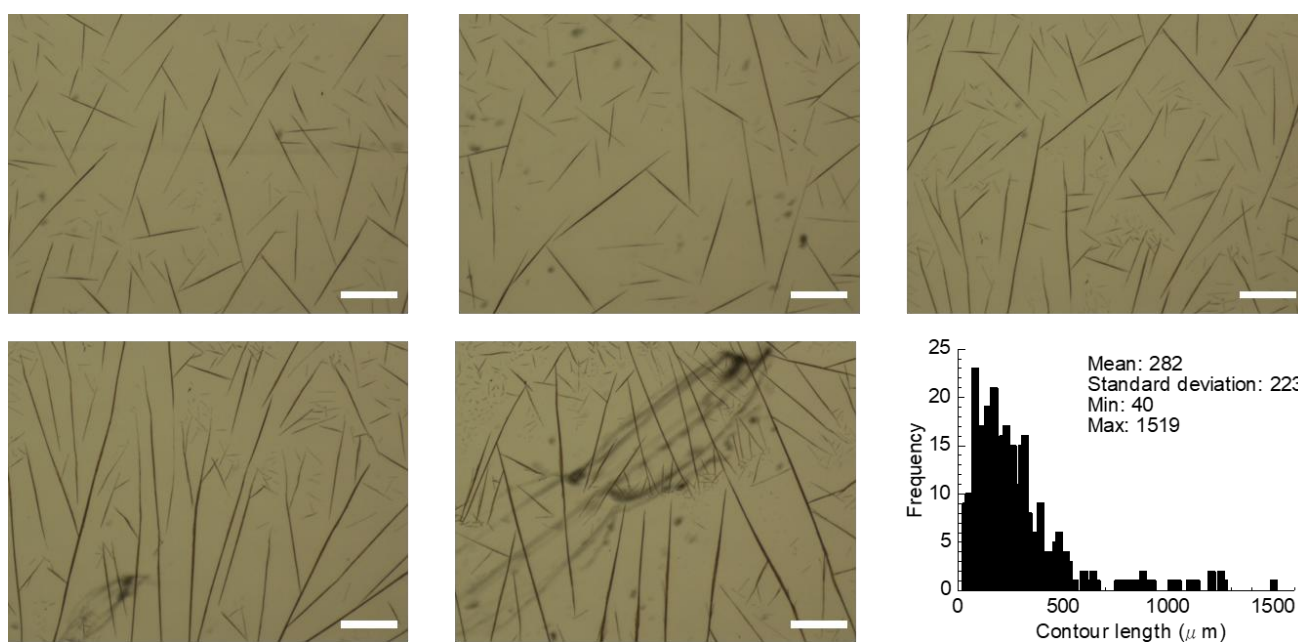


Figure S19. Optical microscopy images of the C_{60} /poly8 composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of poly8 ($M_n = 28.1$ kDa, $M_w/M_n = 1.11$). Scale bars, 200 μm , $N = 390$.

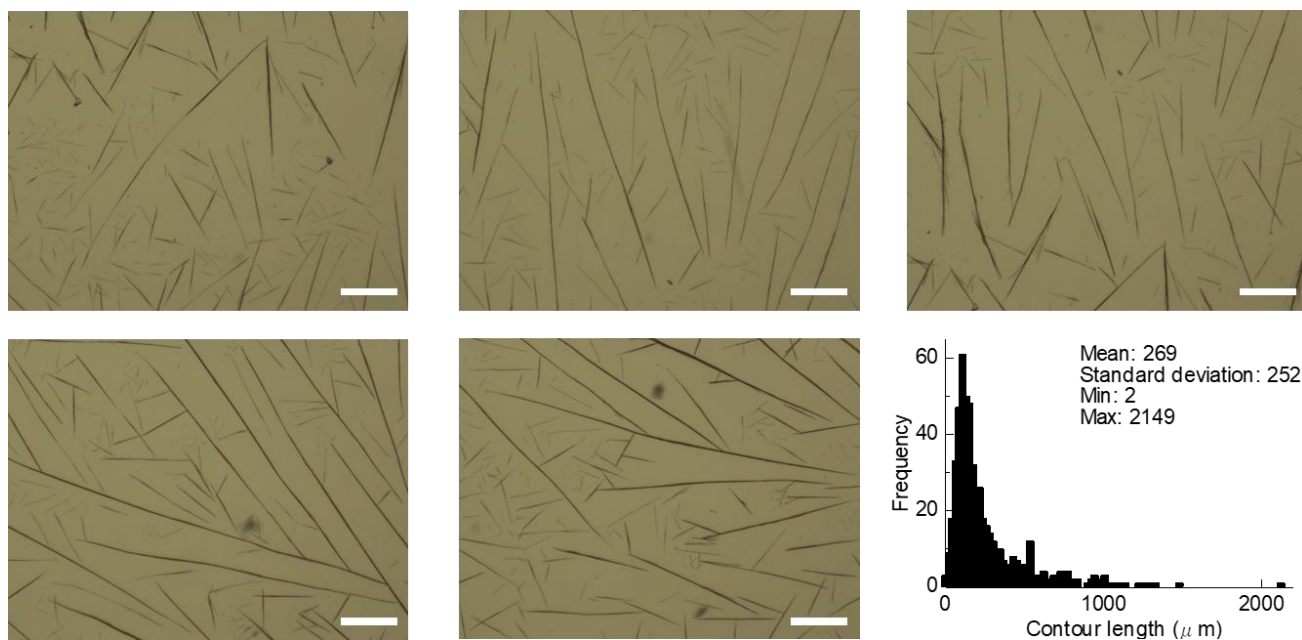


Figure S20. Optical microscopy images of the C_{60} / **poly8** composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of **poly8** ($M_n = 29.4$ kDa, $M_w/M_n = 1.10$). Scale bars, 200 μm , $N = 544$.

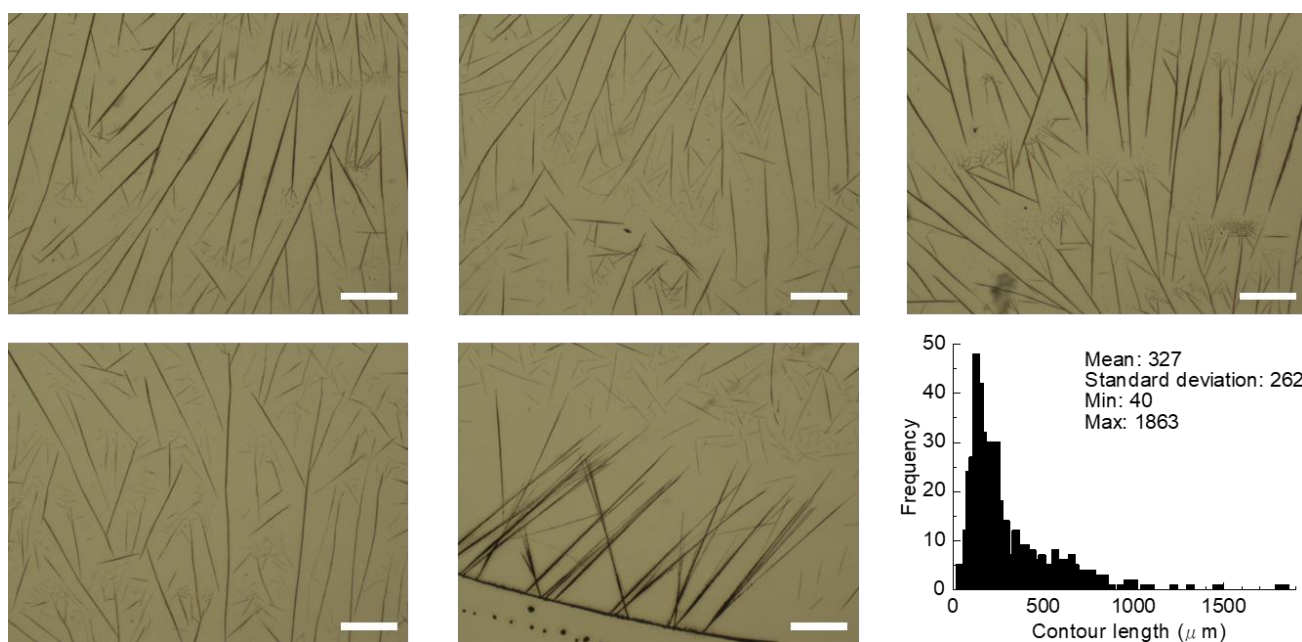


Figure S21. Optical microscopy images of the C_{60} / **poly8** composite film and the corresponding histogram for the length of C_{60} whiskers in the presence of **poly8** ($M_n = 30.4$ kDa, $M_w/M_n = 1.10$). Scale bars, 200 μm , $N = 515$.

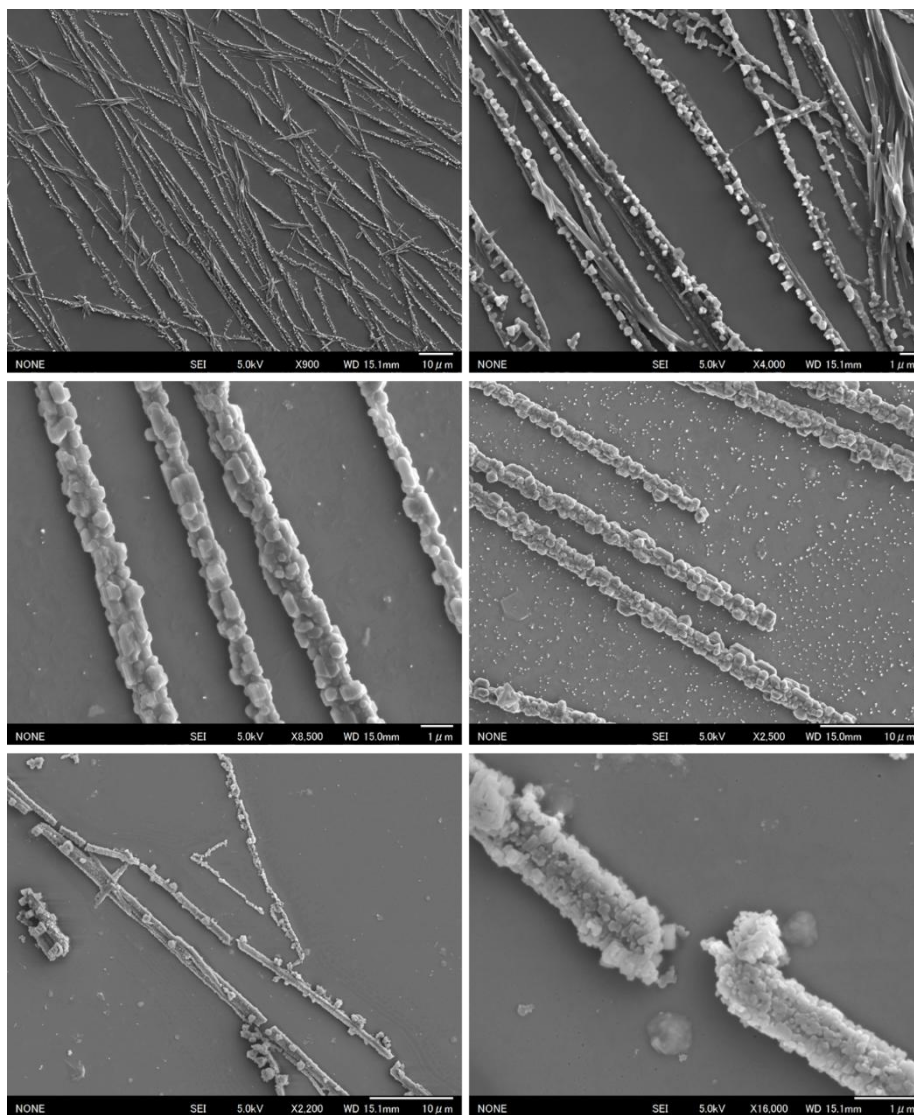


Figure S22. SEM images of C₆₀ fibre prepared from C₆₀/poly12 toluene solution.

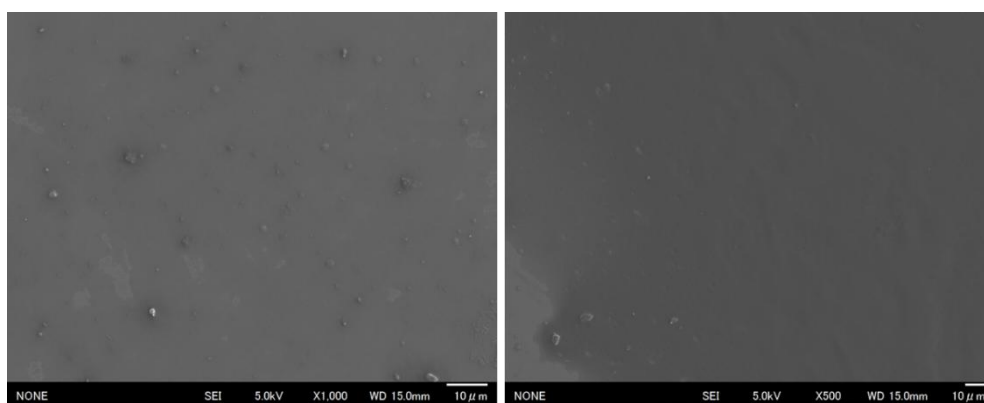


Figure S23. SEM images of pure poly12 film.

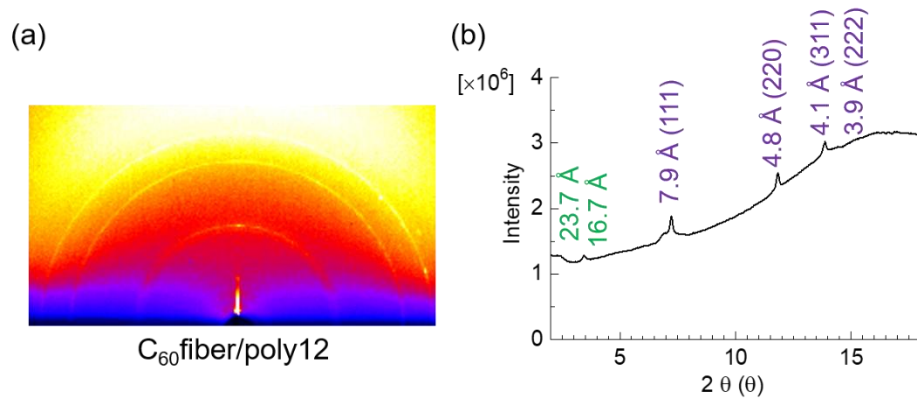


Figure S24. GIXRD for C_{60} fibre prepared from C_{60} /poly12 solution: (a) diffraction pattern and (b) the corresponding $2\theta/\theta$ profile.

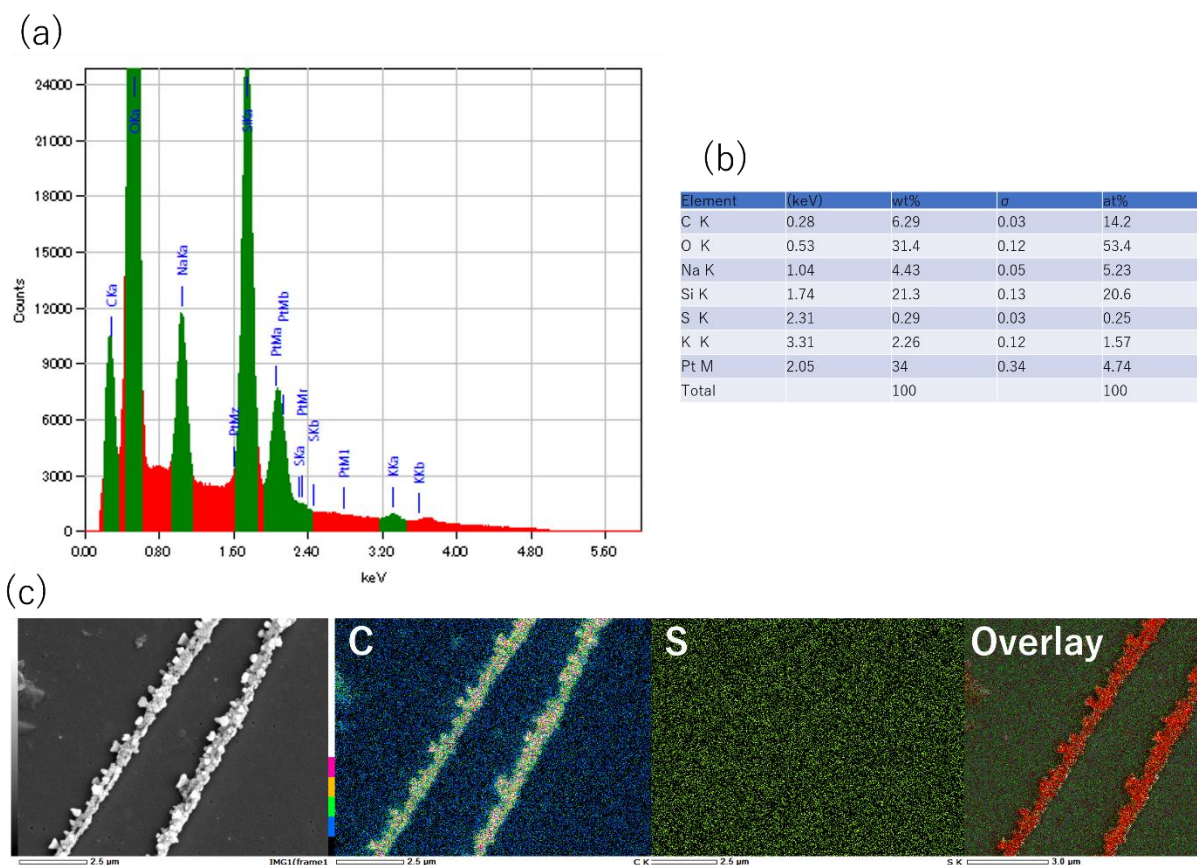


Figure S25. SEM-EDX measurement for hexane-washed C_{60} /poly12 film. (a) EDX spectra, (b) element composition, and (c) element mapping.

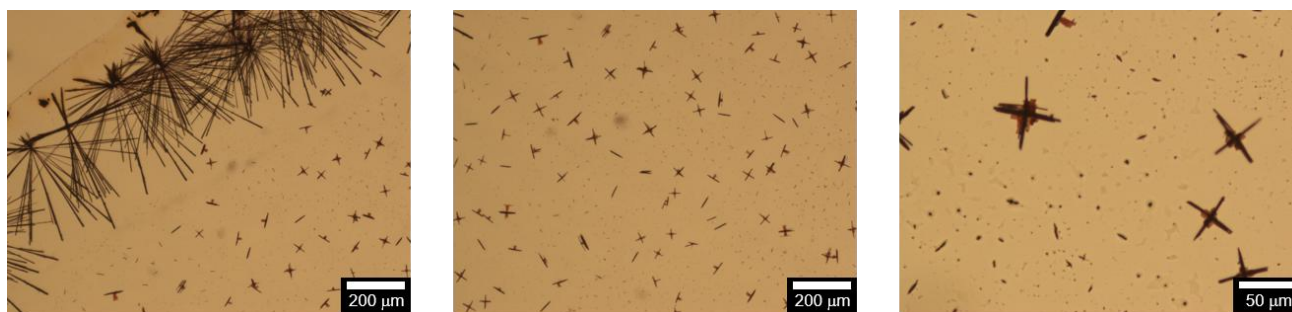


Figure S26. Additional OM images of C₇₀/poly12 composite films.

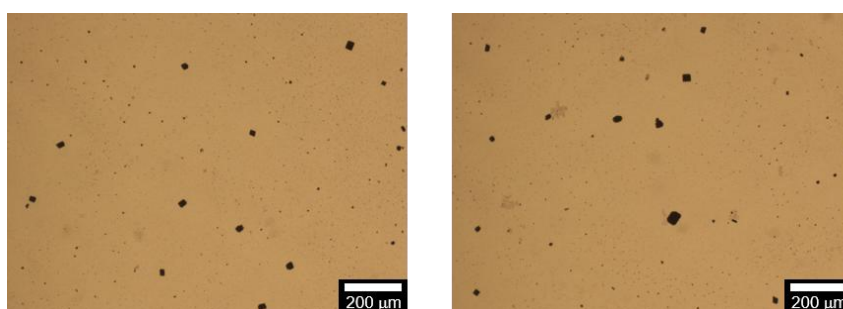


Figure S27. OM images of C₇₀ crystals prepared from pure C₇₀ toluene solution (1.0 mg/mL).

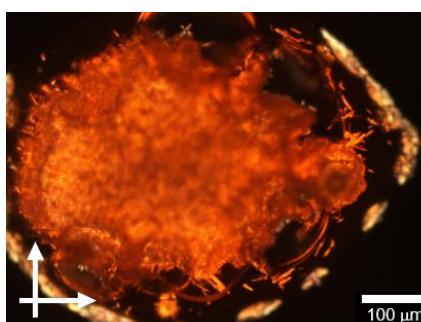


Figure S28. POM images of Rubrene crystals prepared from pure Rubrene toluene solution (1.0 mg/mL) and subsequent thermal annealing at 120 °C for 30 min.

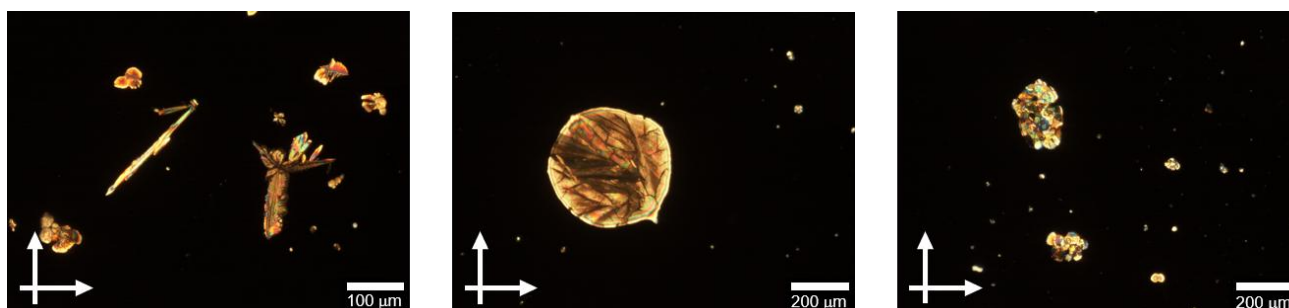


Figure S29. POM images of TPE crystals prepared from pure TPE toluene solution (1.0 mg/mL).

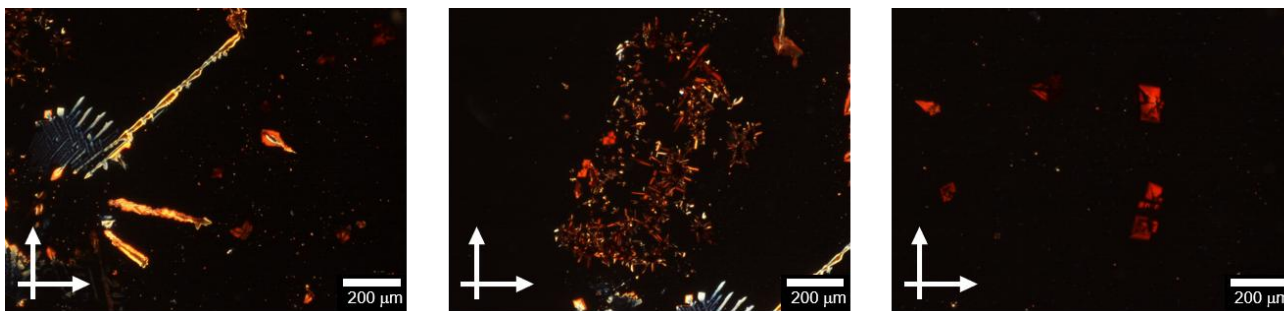


Figure S30. POM images of TPP crystals prepared from pure TPP toluene solution (1.0 mg/mL).

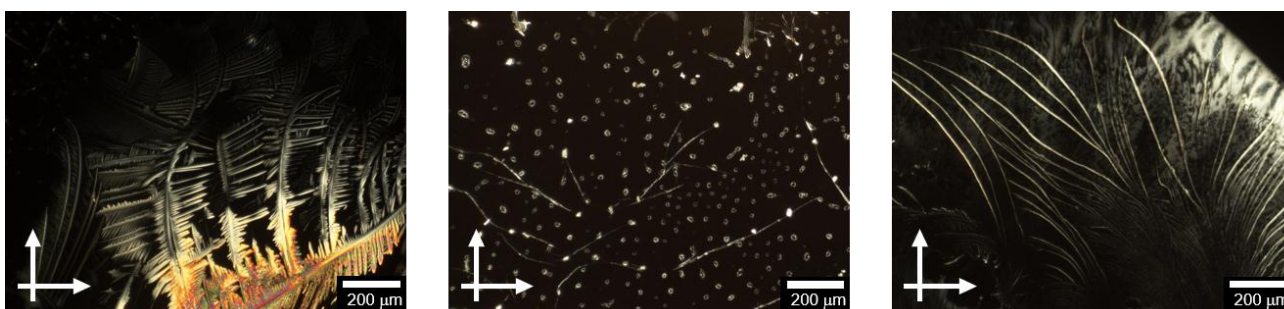


Figure S31. Additional POM images of TPE/**poly12** composite films.

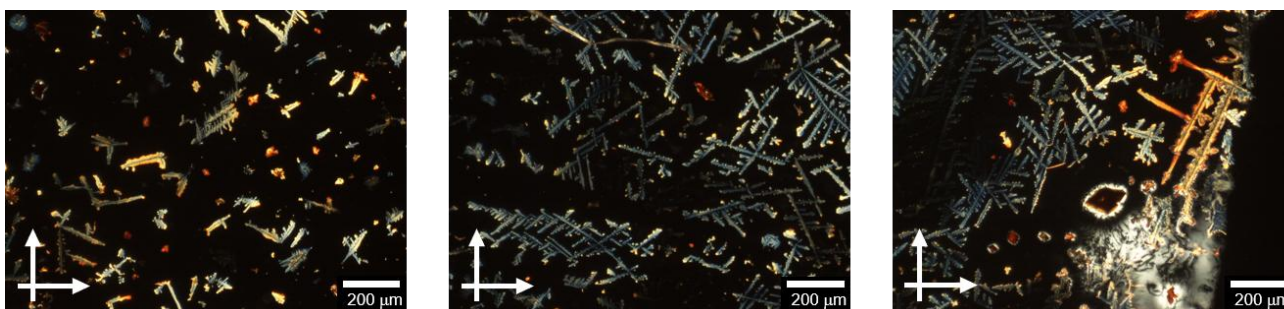


Figure S32. Additional POM images of TPP/**poly12** composite films.

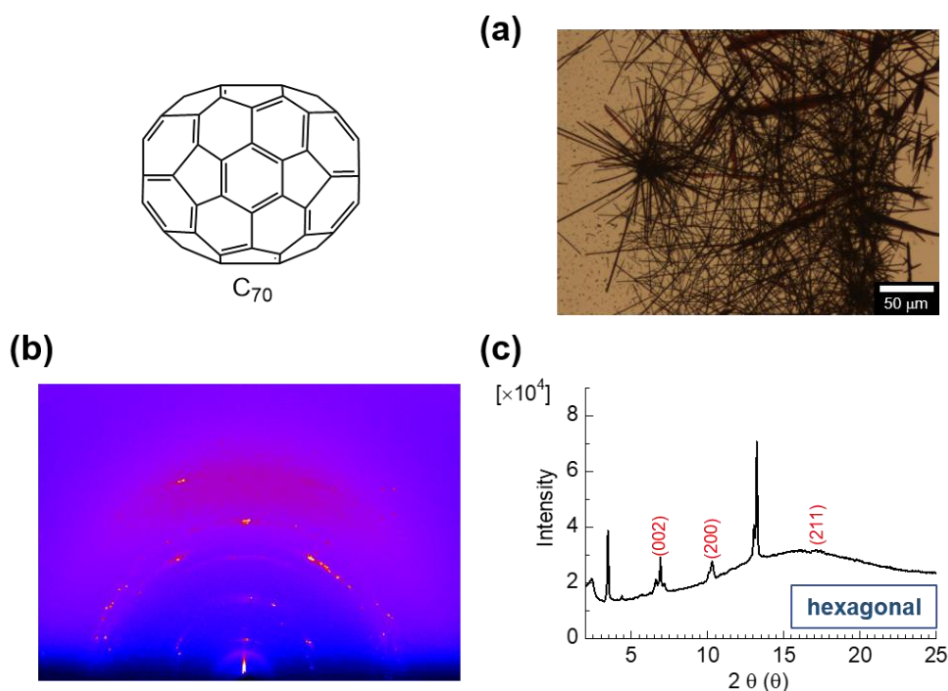


Figure S33. (a) Optical microscopy image and (b,c) GIXRD measurements for C₇₀/poly12 film (wavelength of X-ray: 0.9965Å). The broad halo at $2\theta \sim 16^\circ$ is due to the amorphous diffraction of the glass substrate.

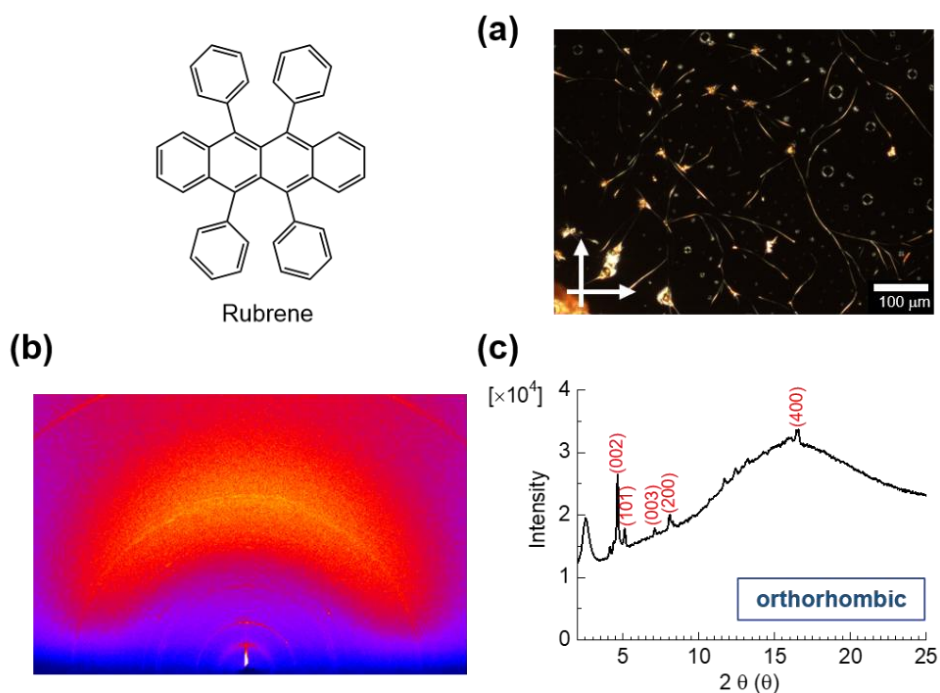


Figure S34. (a) Polarising optical microscopy image and (b,c) GIXRD measurements for rubrene/poly12 film (wavelength of X-ray: 0.9965Å). The film was annealed at 120 °C for 30 min in air after toluene solvent drying. The broad halo at $2\theta \sim 16^\circ$ is due to the amorphous diffraction of the glass substrate.

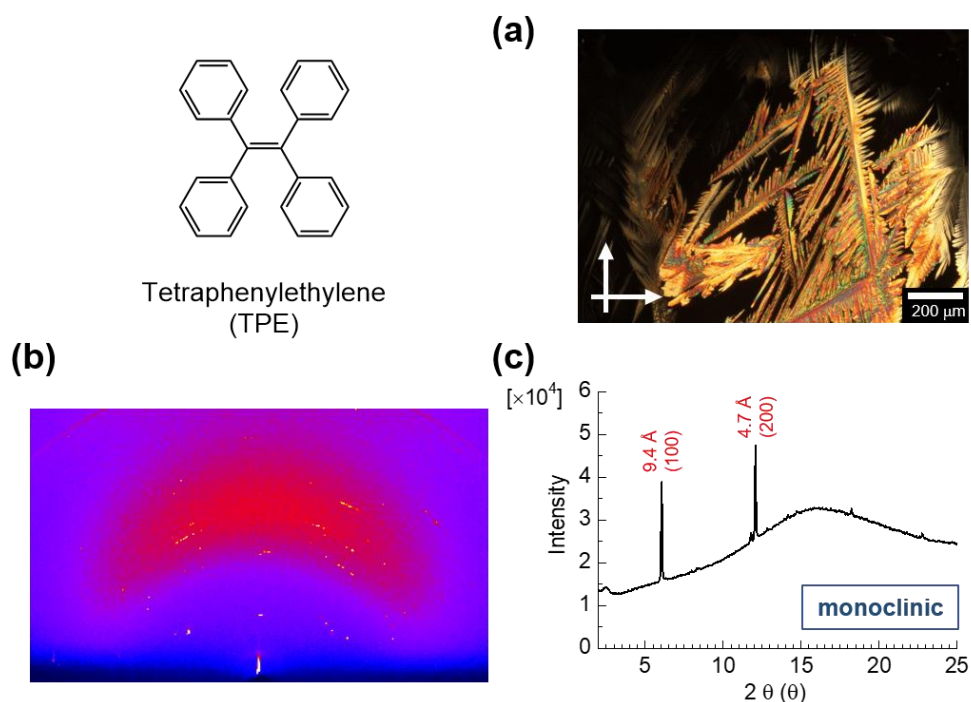


Figure S35. (a) Polarising optical microscopy image and (b,c) GIXRD measurements for TPE/**poly12** film (wavelength of X-ray: 0.9965Å). The broad halo at $2\theta \sim 16^\circ$ is due to the amorphous diffraction of the glass substrate.

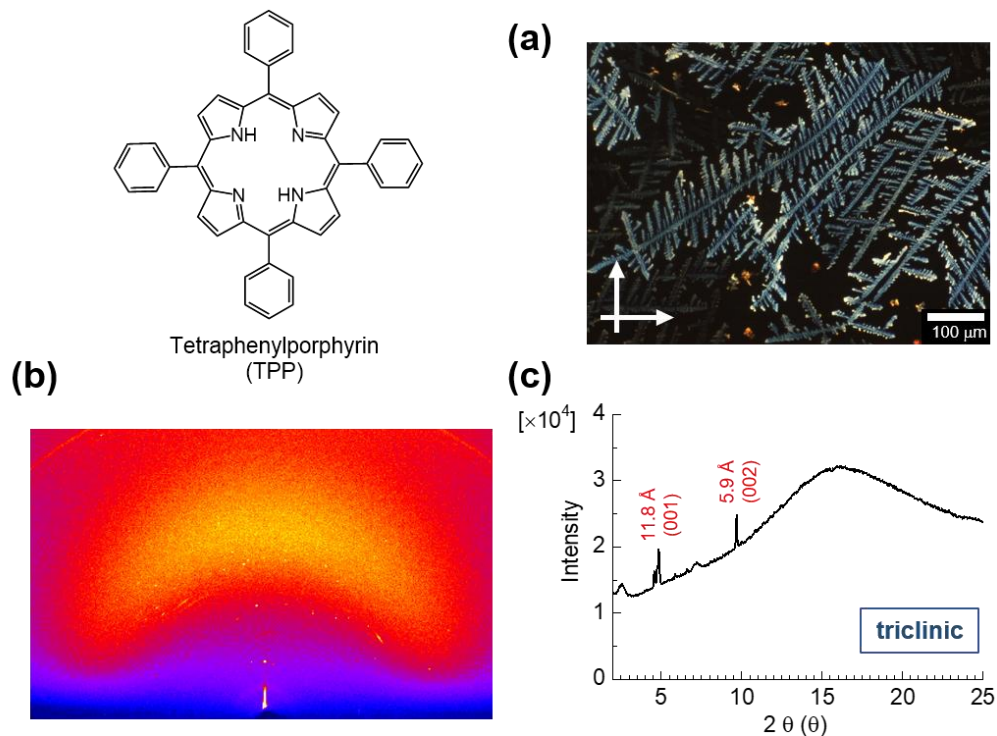


Figure S36. (a) Polarising optical microscopy image and (b,c) GIXRD measurements for TPP/**poly12** film (wavelength of X-ray: 0.9965Å). The broad halo at $2\theta \sim 16^\circ$ is due to the amorphous diffraction of the glass substrate.

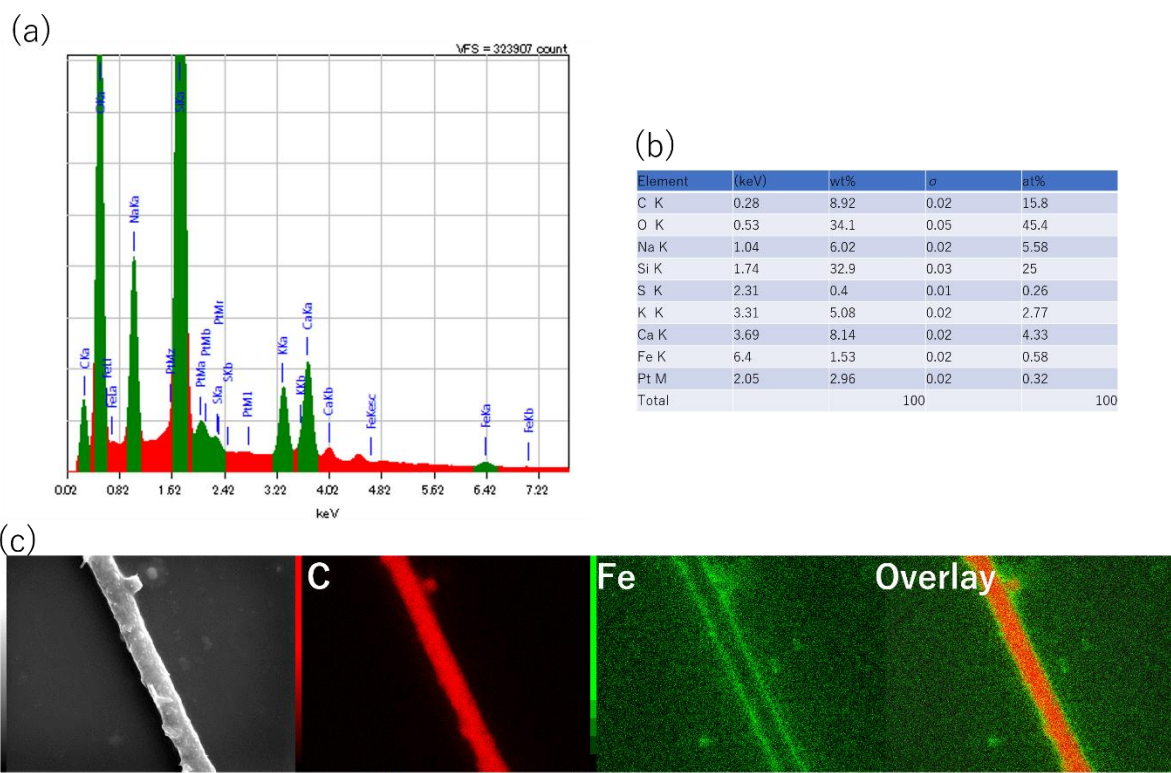


Figure S40. SEM-EDX measurement for hexane-washed FeNP/C₆₀/poly12 film. (a) EDX spectra, (b) element composition, and (c) element mapping.

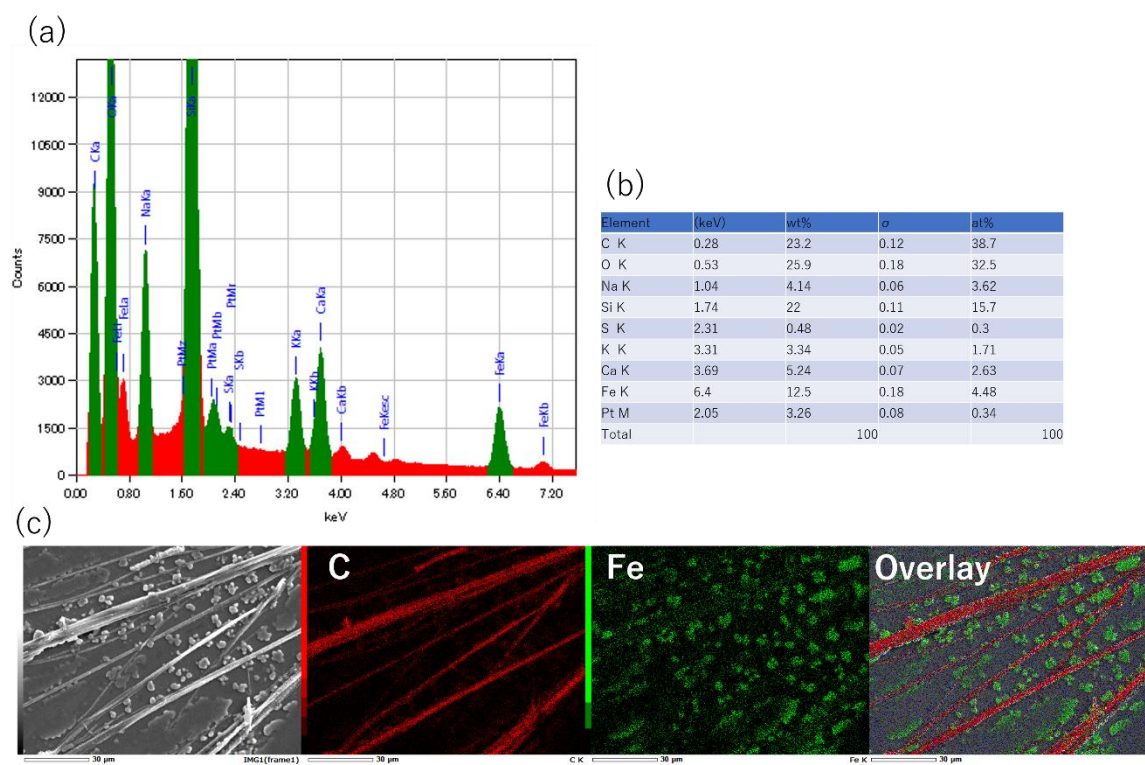


Figure S41. SEM-EDX measurement for hexane-washed FeNP/C₆₀/poly12 film. (a) EDX spectra, (b) element composition, and (c) element mapping

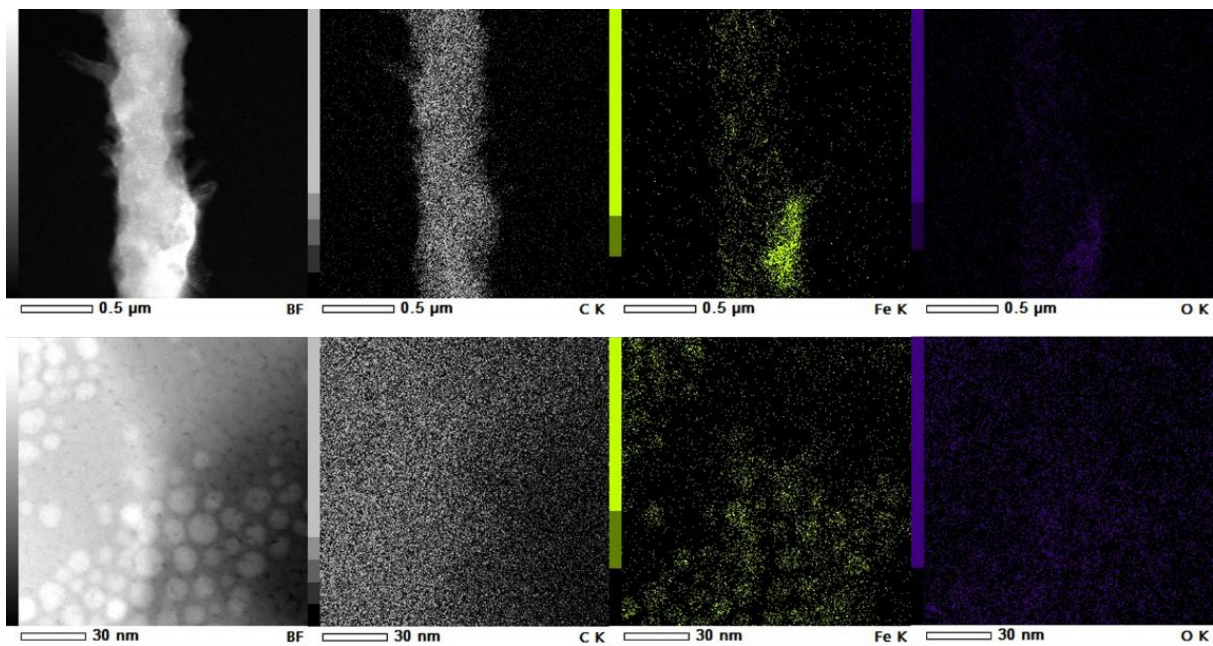
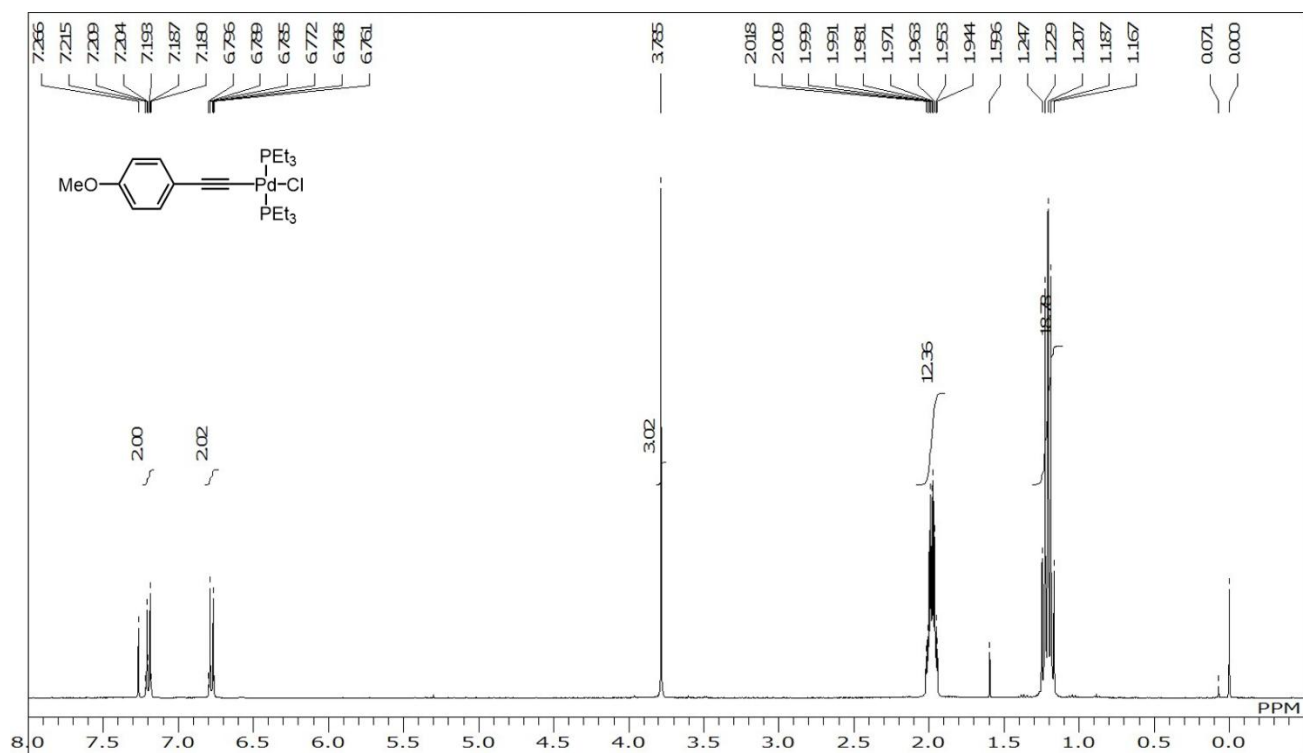
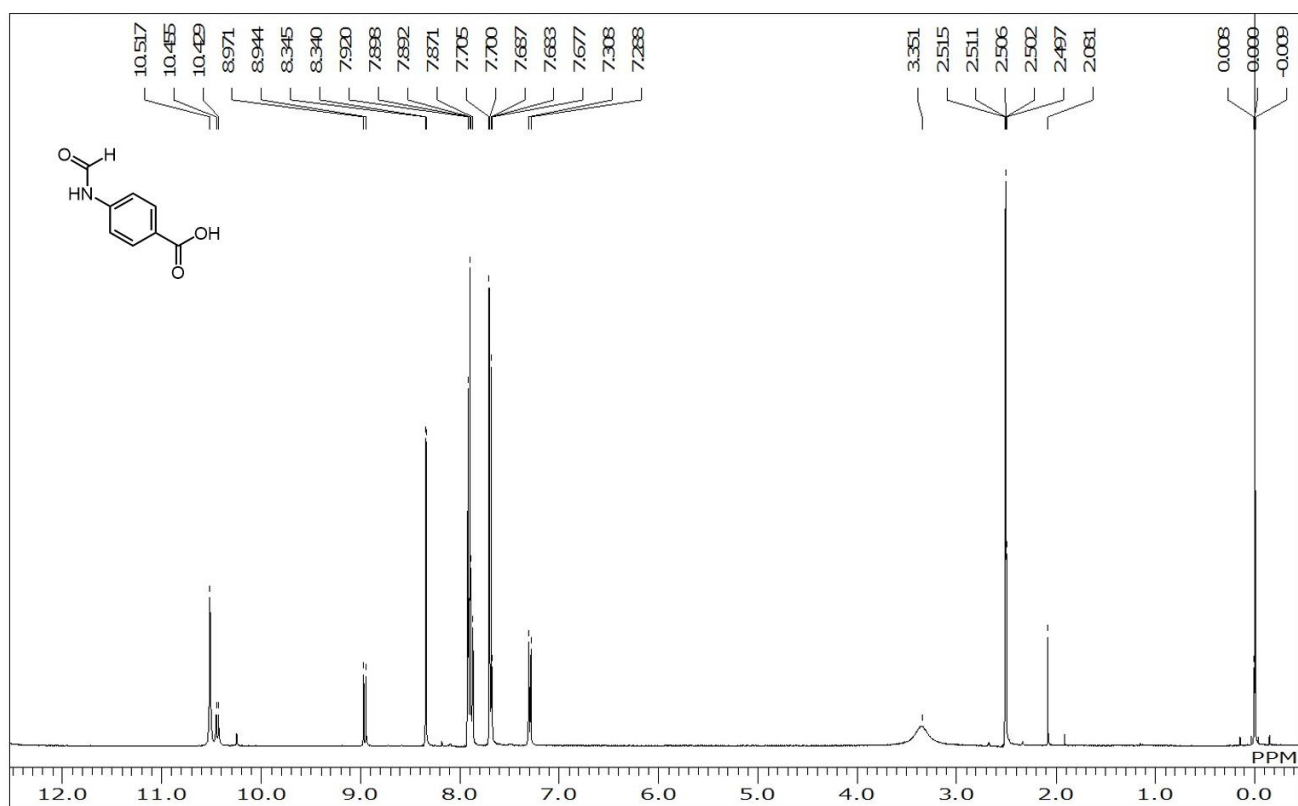


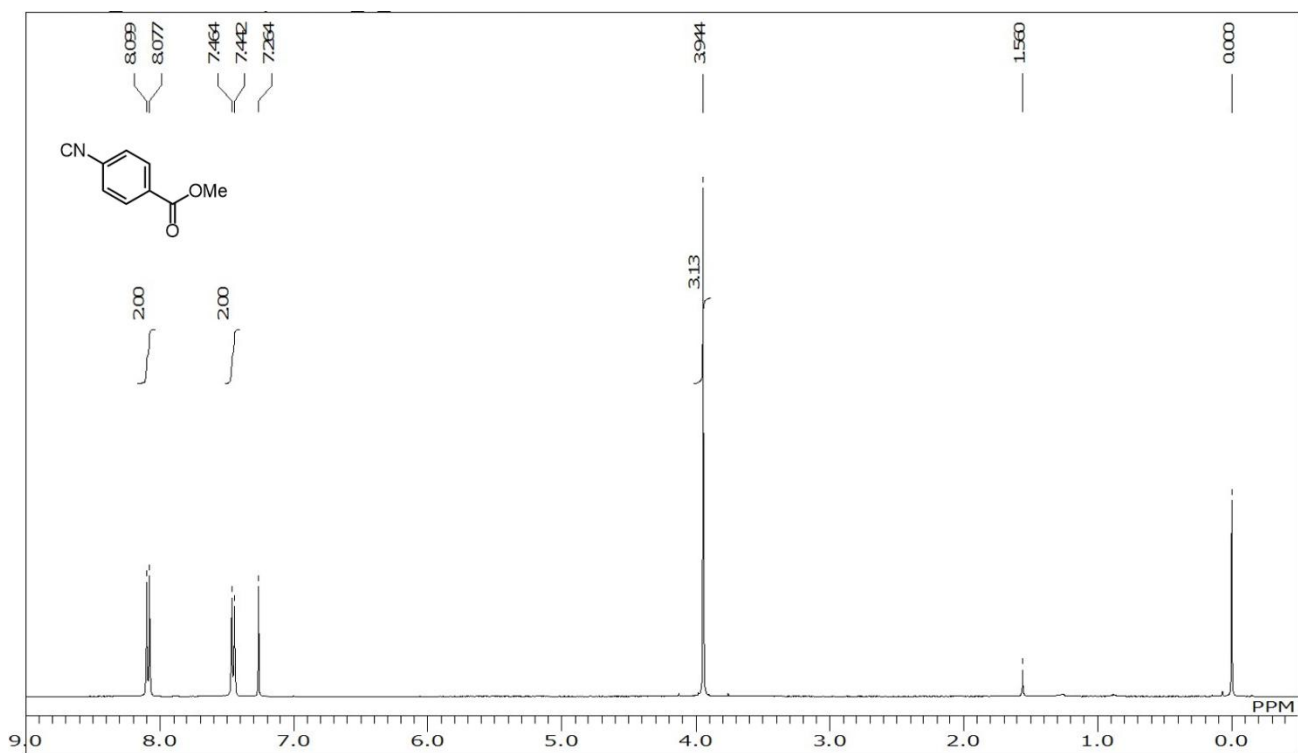
Figure S42. TEM-EDS measurements for C₆₀/FeNP hybrid fiber.



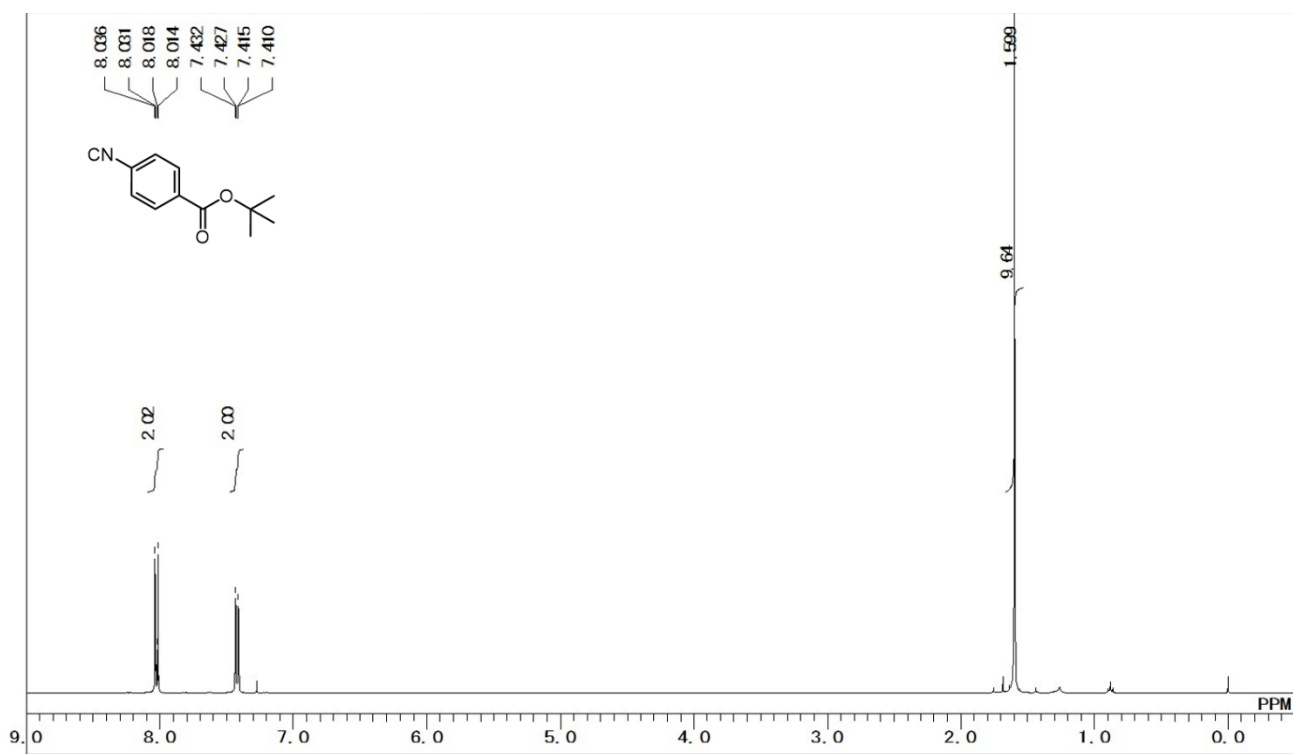
¹H NMR of 4-methoxy-phenylethynyl Pd complex (400Hz, CDCl₃).



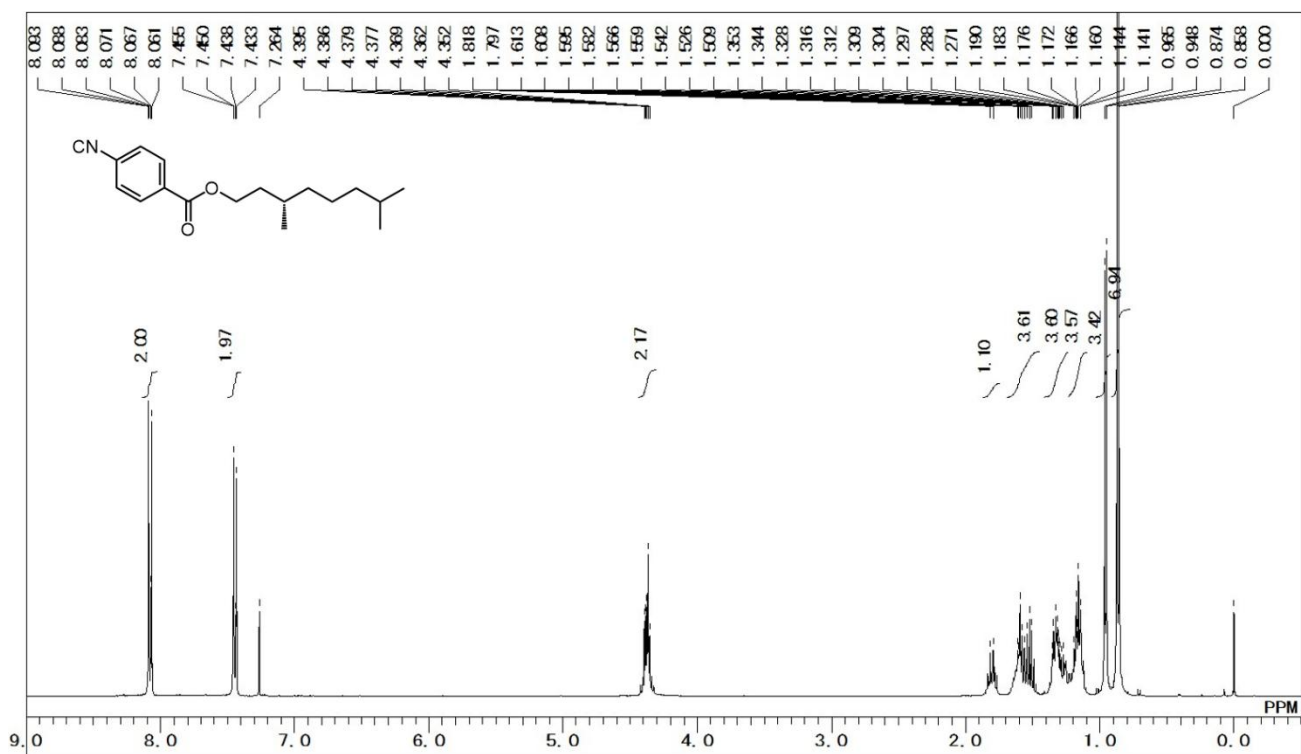
¹H NMR of 4-formamidobenzoic acid (400Hz, DMSO-d₆).



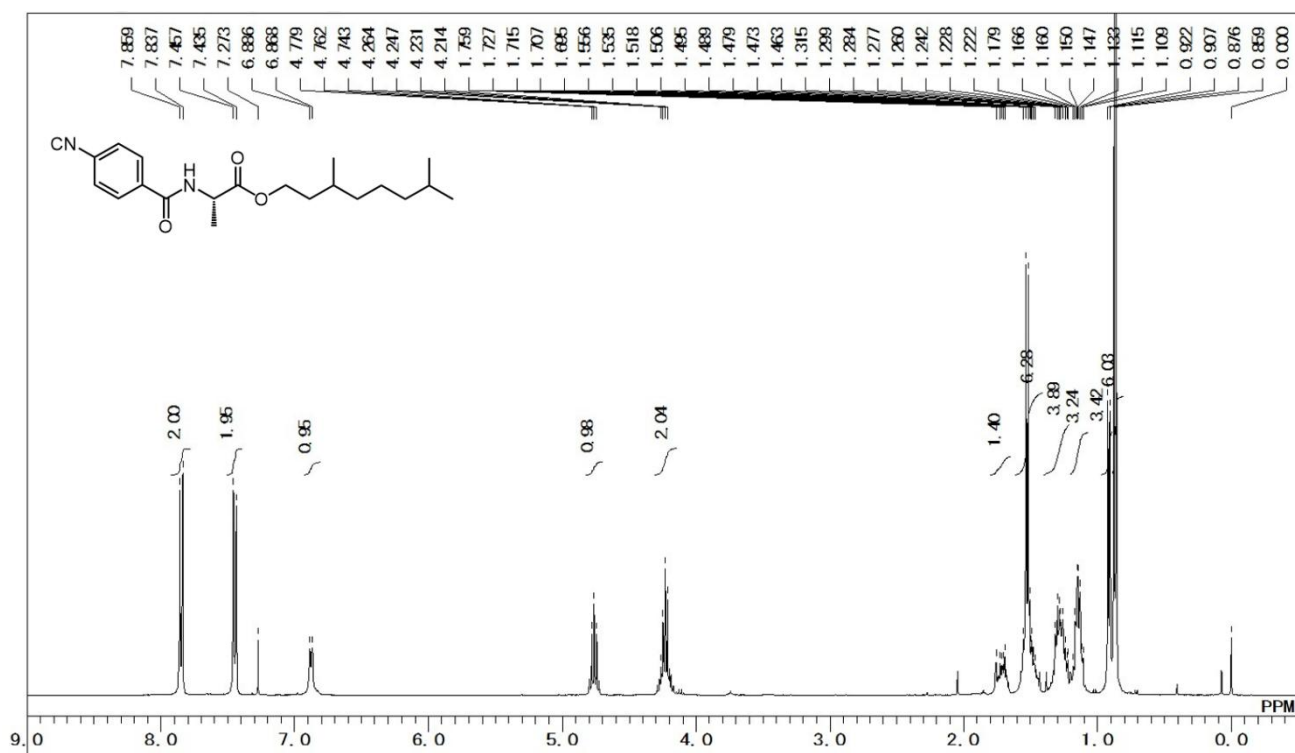
^1H NMR of methyl-4-isocyanobenzoate (1) (400Hz, CDCl_3).



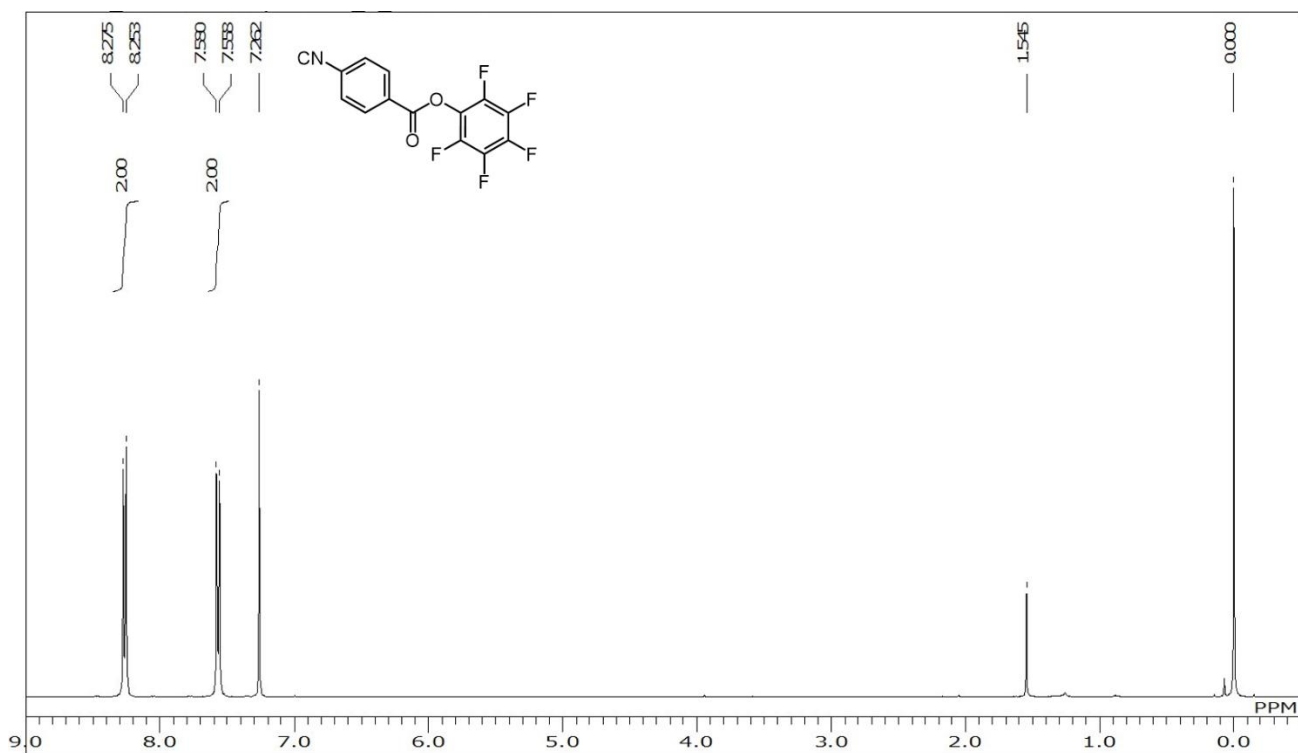
^1H NMR of *tert*-butyl-4-isocyanobenzoate (2) (400Hz, CDCl_3).



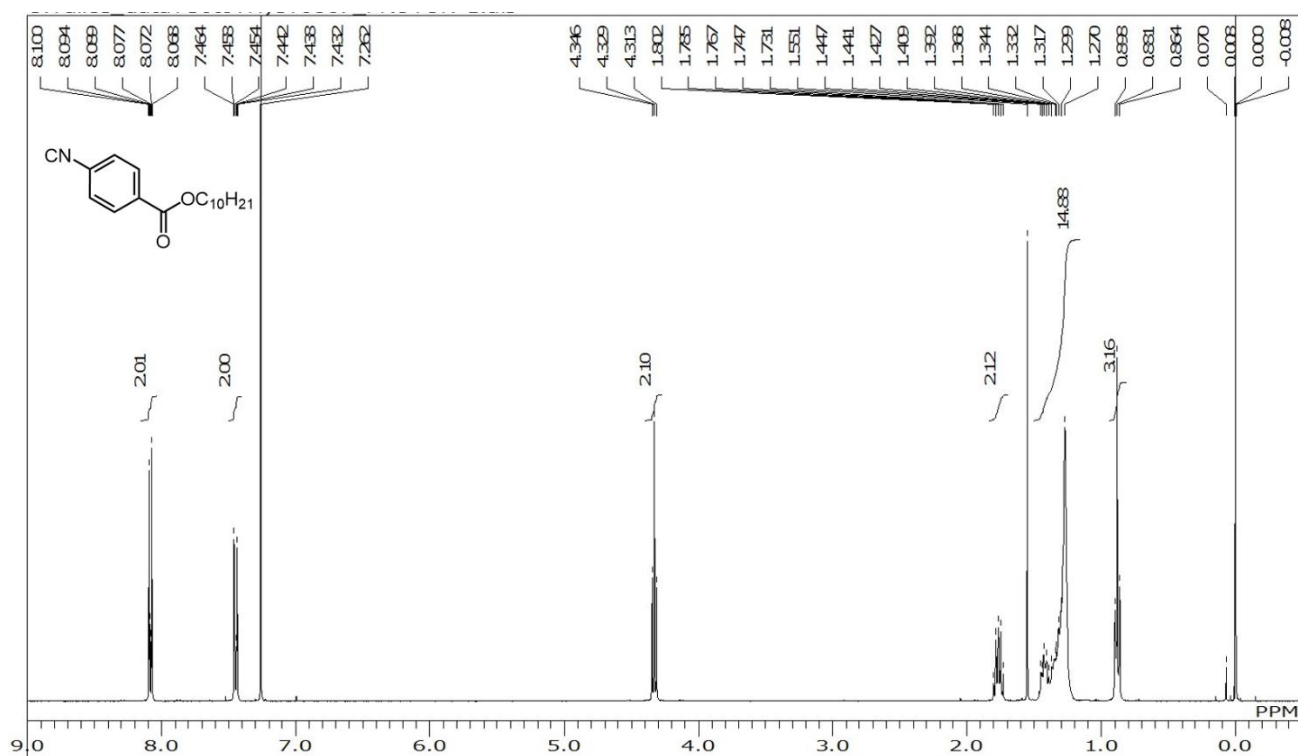
¹H NMR of ((3S)-3,7-Dimethyloctyl)-4-isocyanobenzoate (5) (400Hz, CDCl₃).



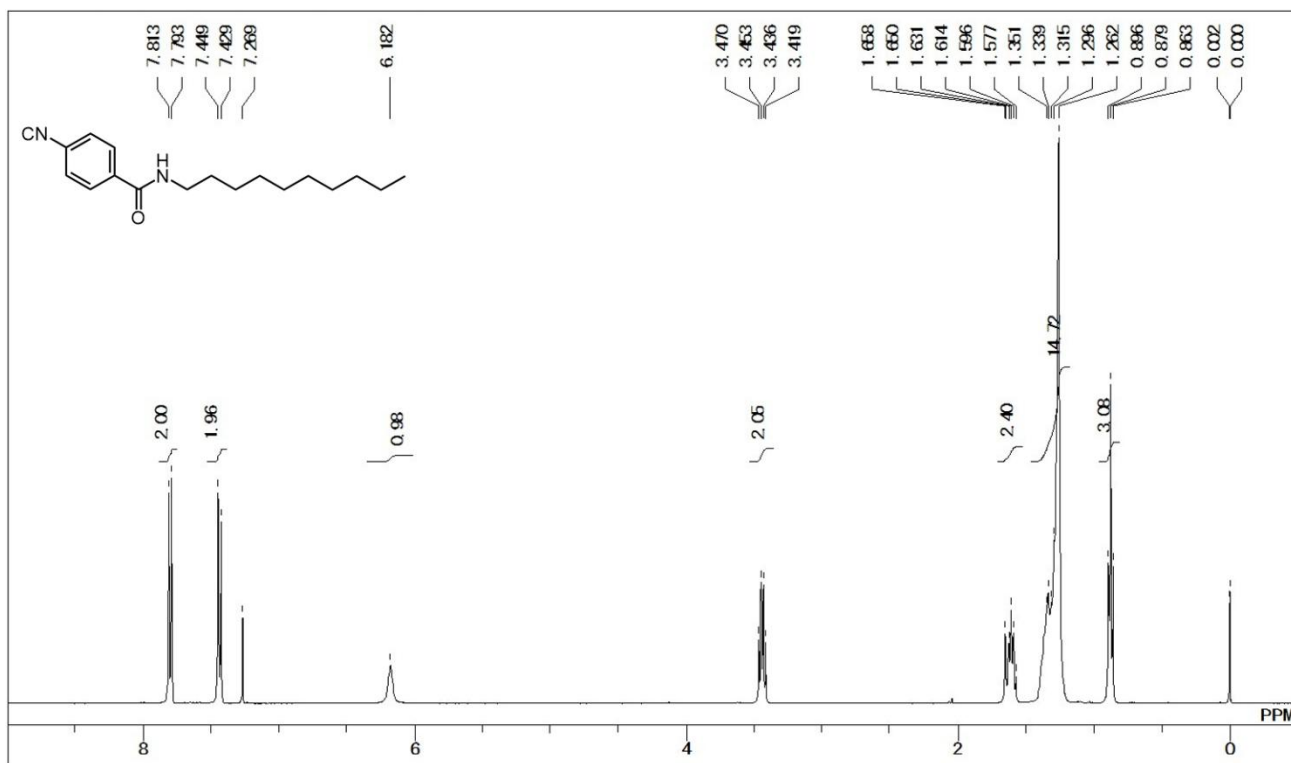
¹H NMR of (L-alanine-based-3,7-dimethyloctylester)-4-isocyanobenzamin (6) (400Hz, CDCl₃).



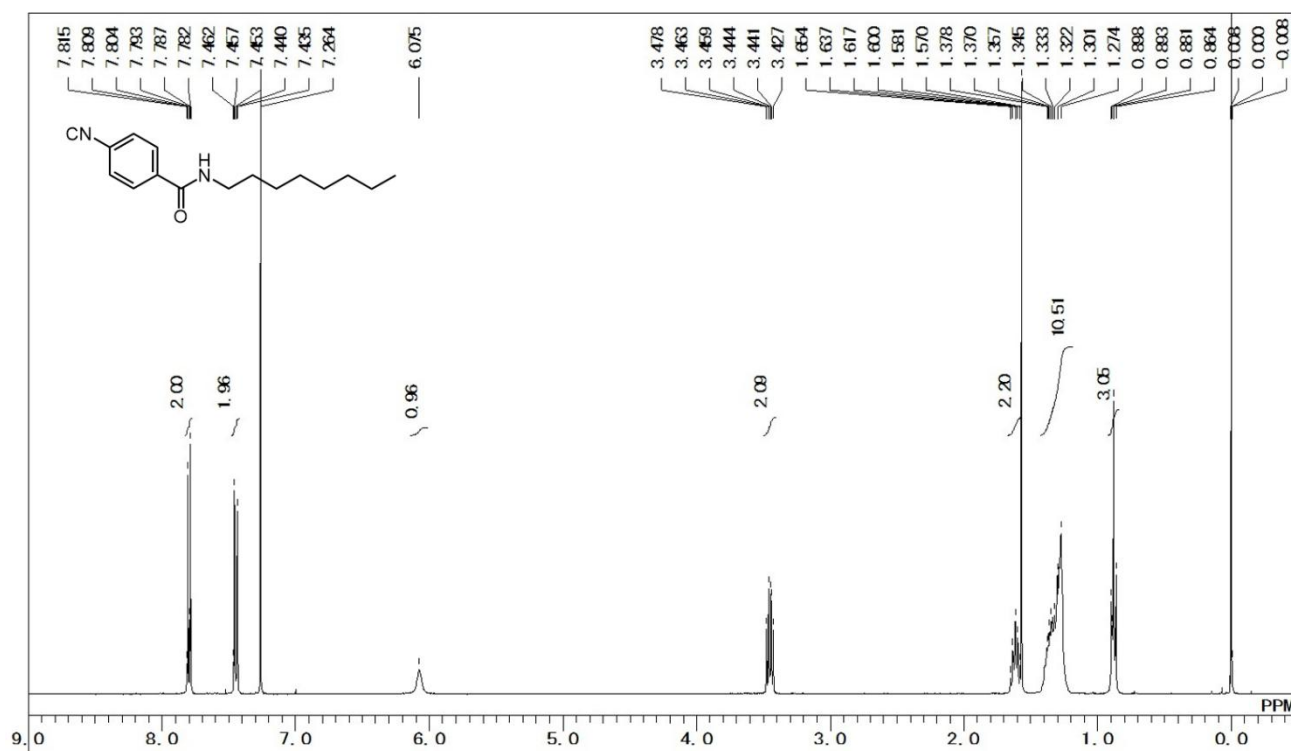
^1H NMR of pentafluorophenyl-4-isocyanobenzoate (7) (400Hz, CDCl_3).



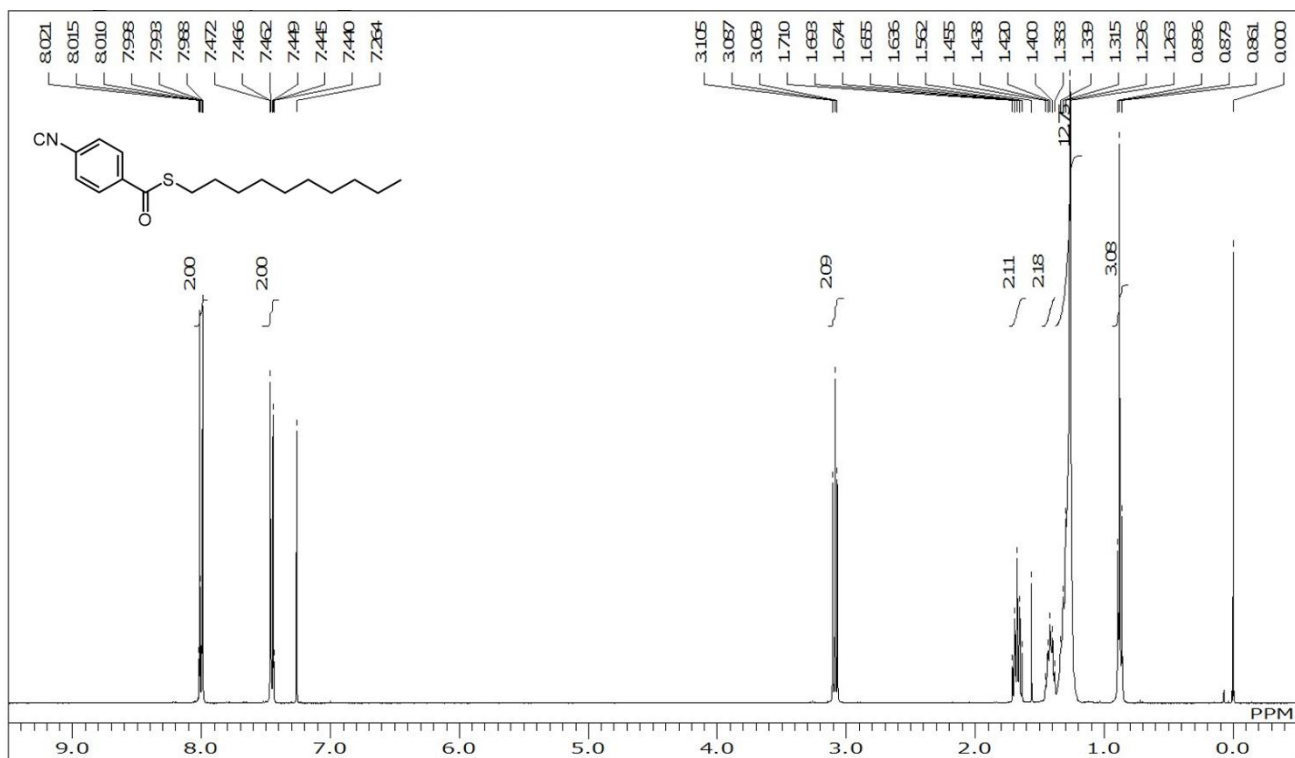
^1H NMR of decyl-4-isocyanobenzoate (8) (400Hz, CDCl_3).



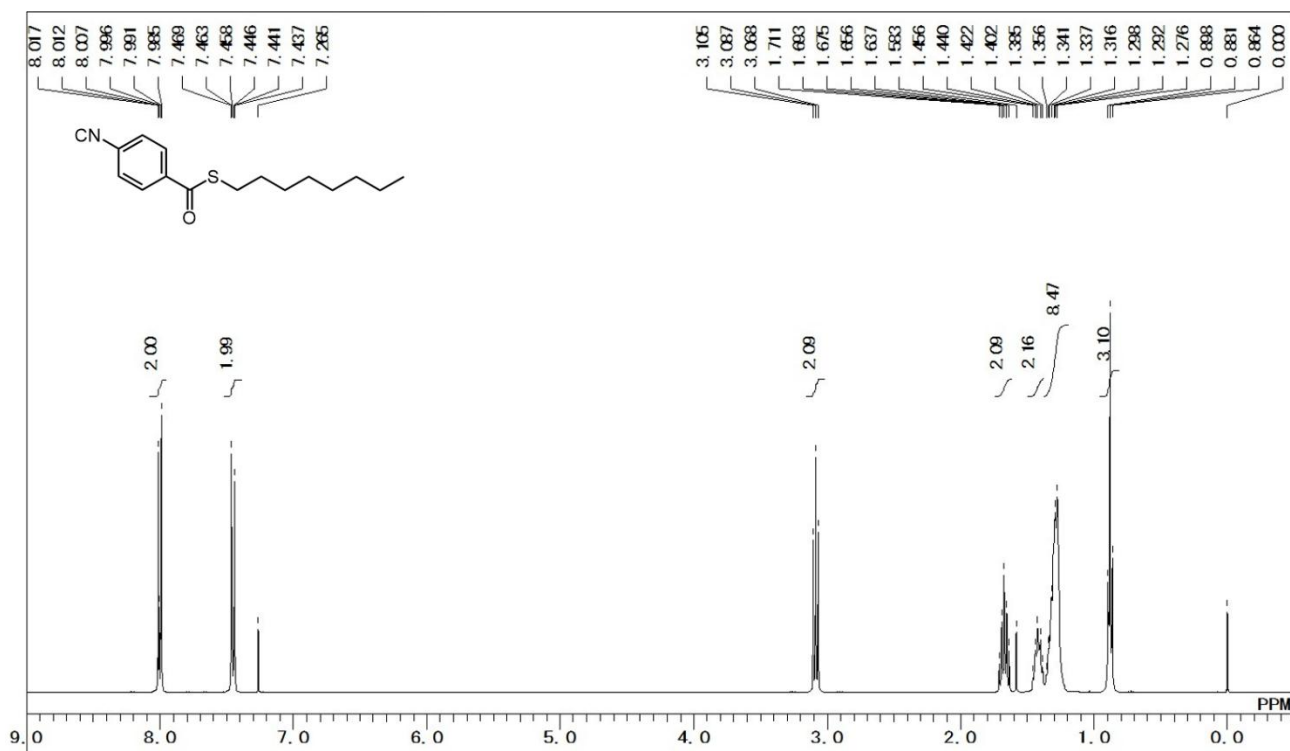
¹H NMR of *N*-decyl-4-isocyanobenzamine (10) (400Hz, CDCl₃).



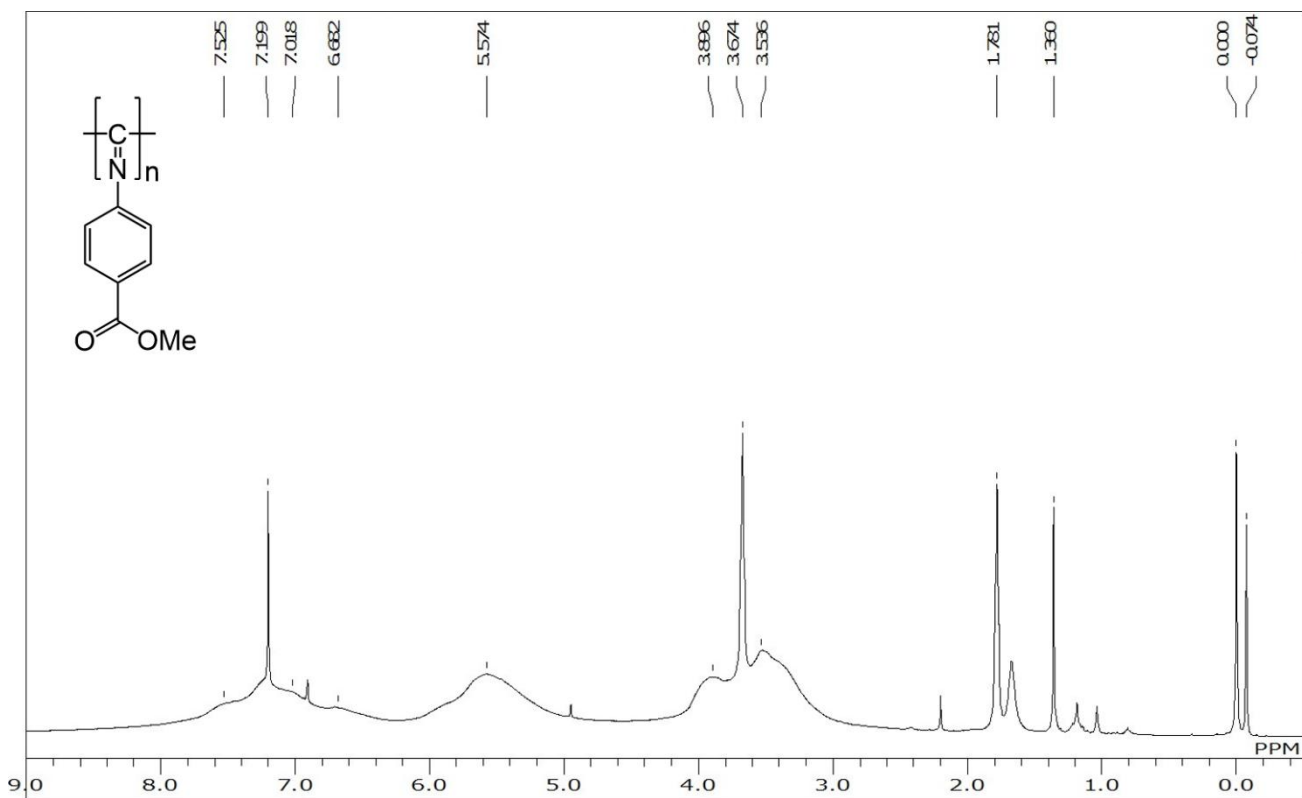
¹H NMR of *N*-octyl-4-isocyanobenzamine (11) (400Hz, CDCl₃).



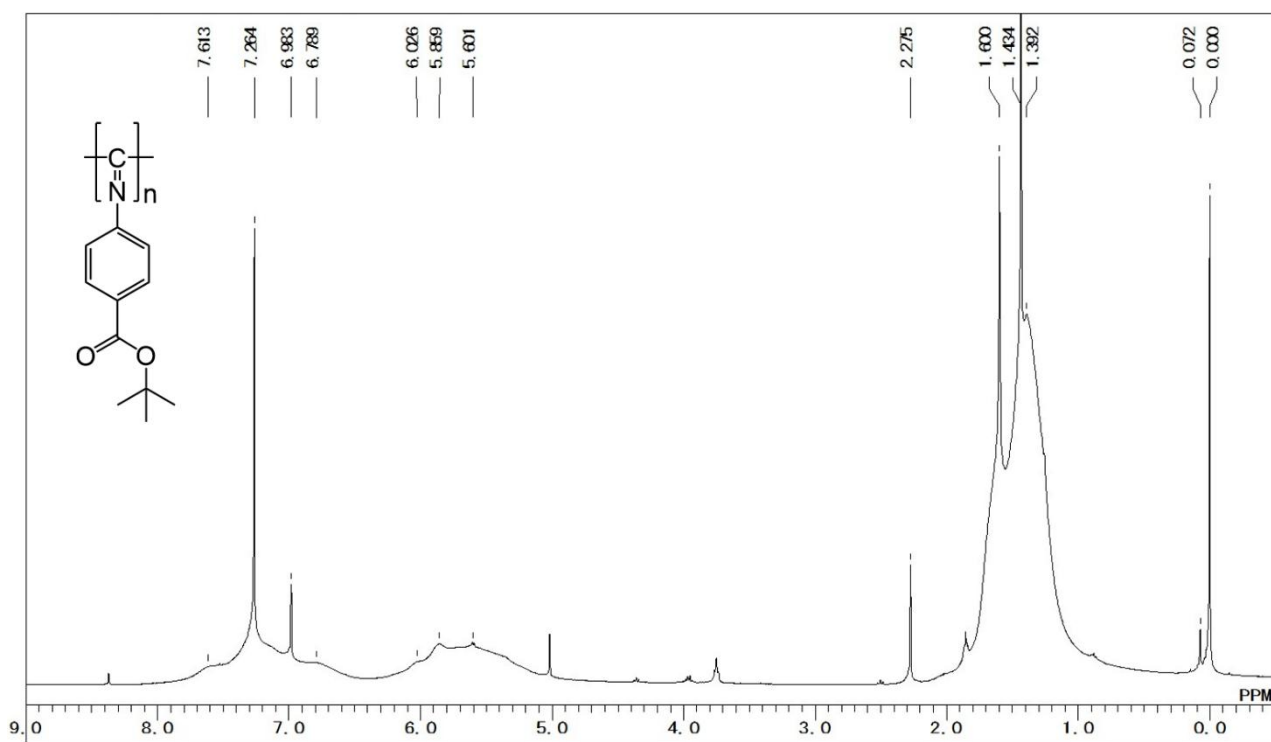
¹H NMR of 4-isocyanobenzoic acid decyl thioester (12) (400Hz, CDCl₃).



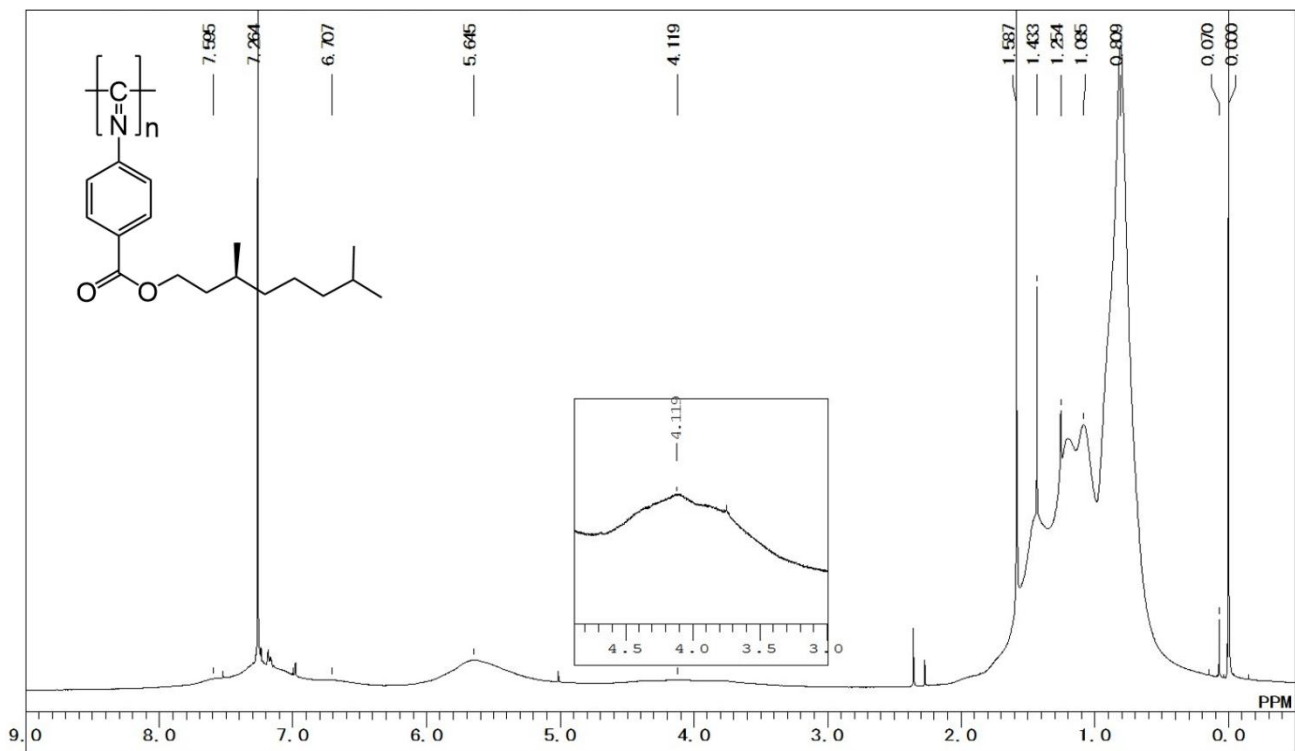
¹H NMR of 4-isocyanobenzoic acid decyl thioester (13) (400Hz, CDCl₃).



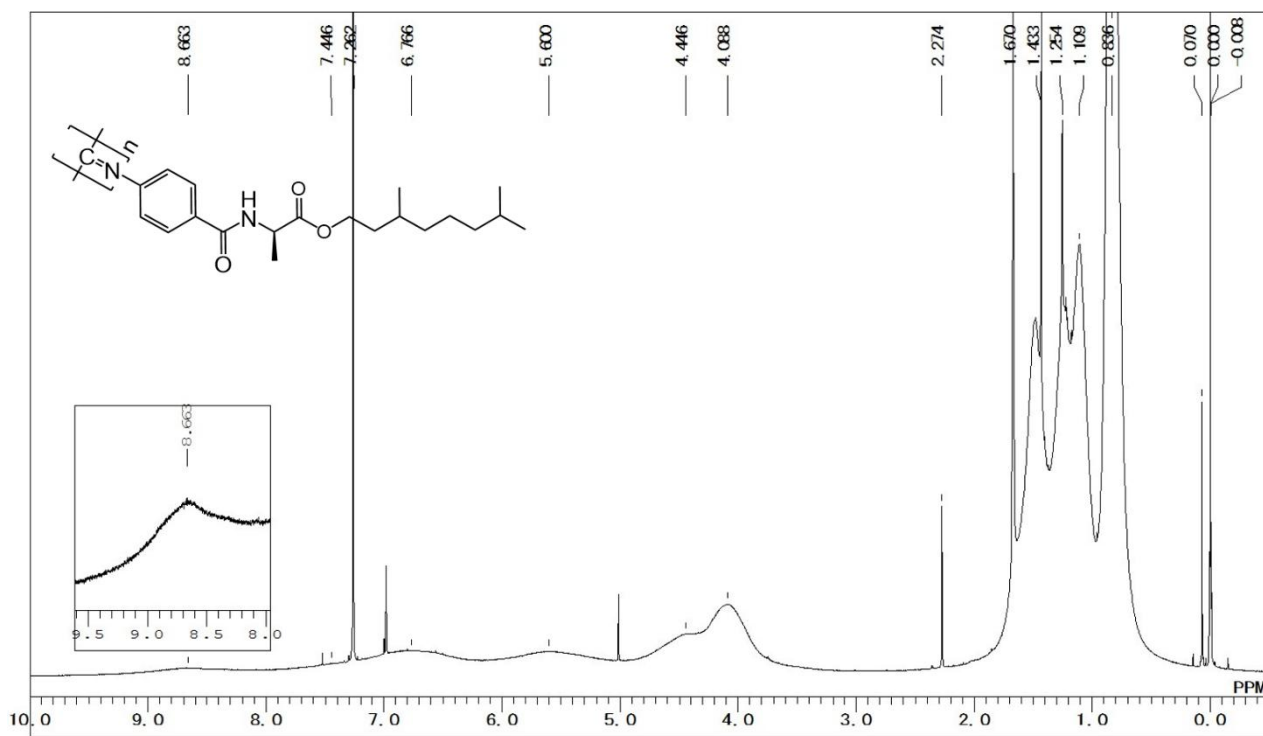
¹H NMR of poly1 (400Hz, CDCl₃).



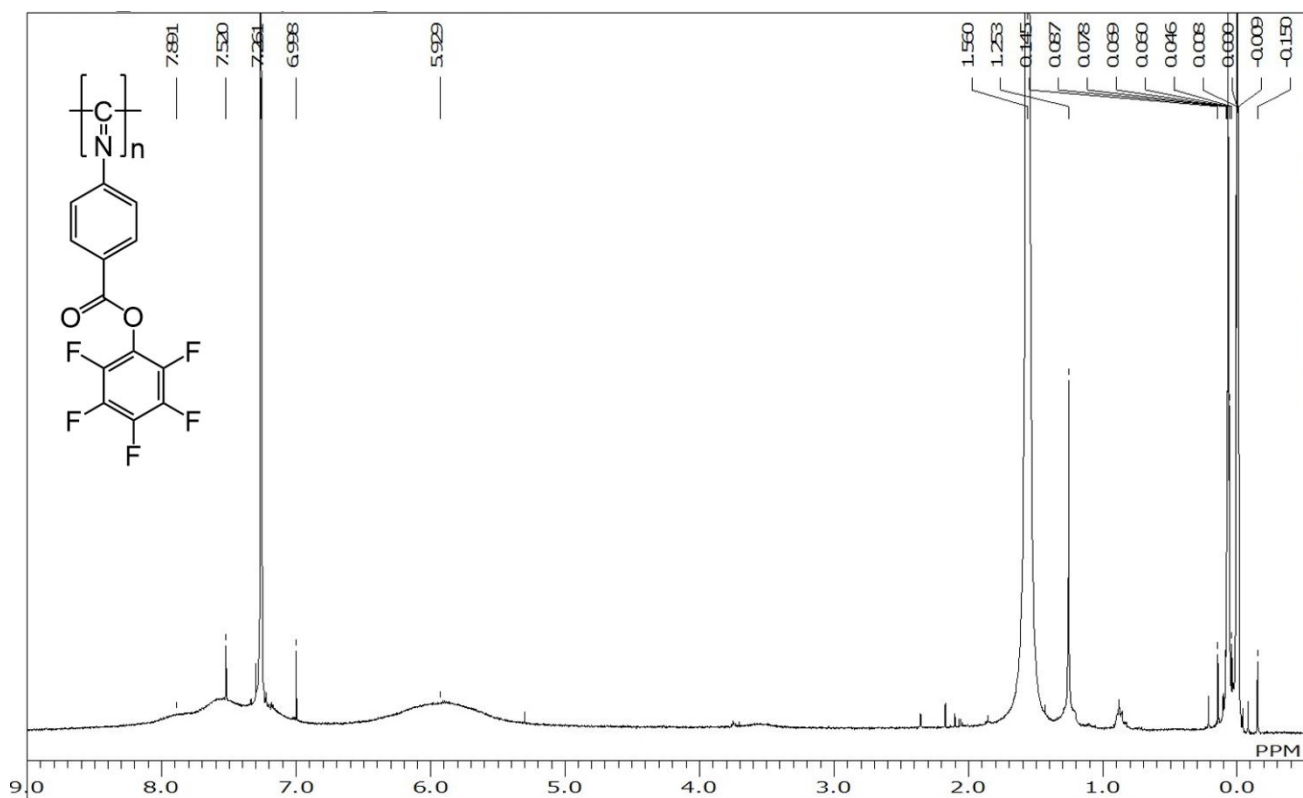
¹H NMR of poly2 (400Hz, CDCl₃).



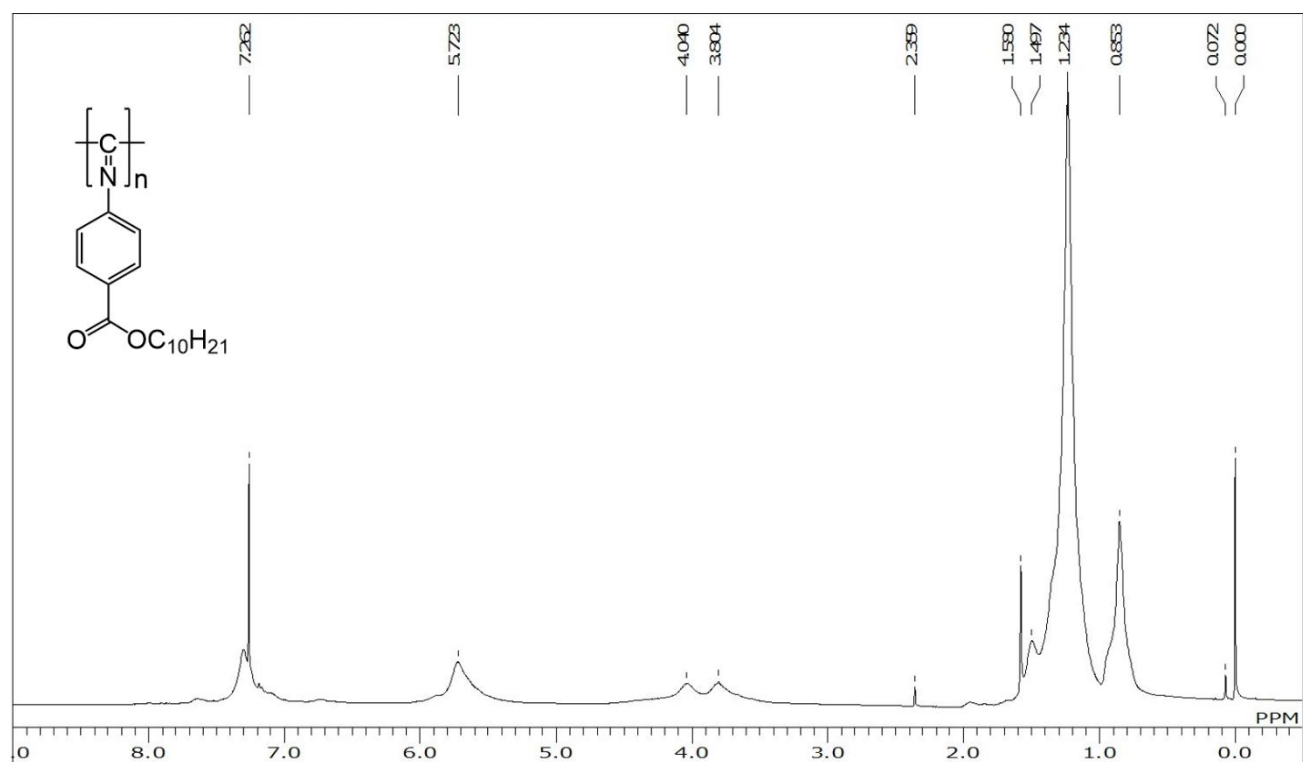
^1H NMR of poly5 (400Hz, CDCl_3).



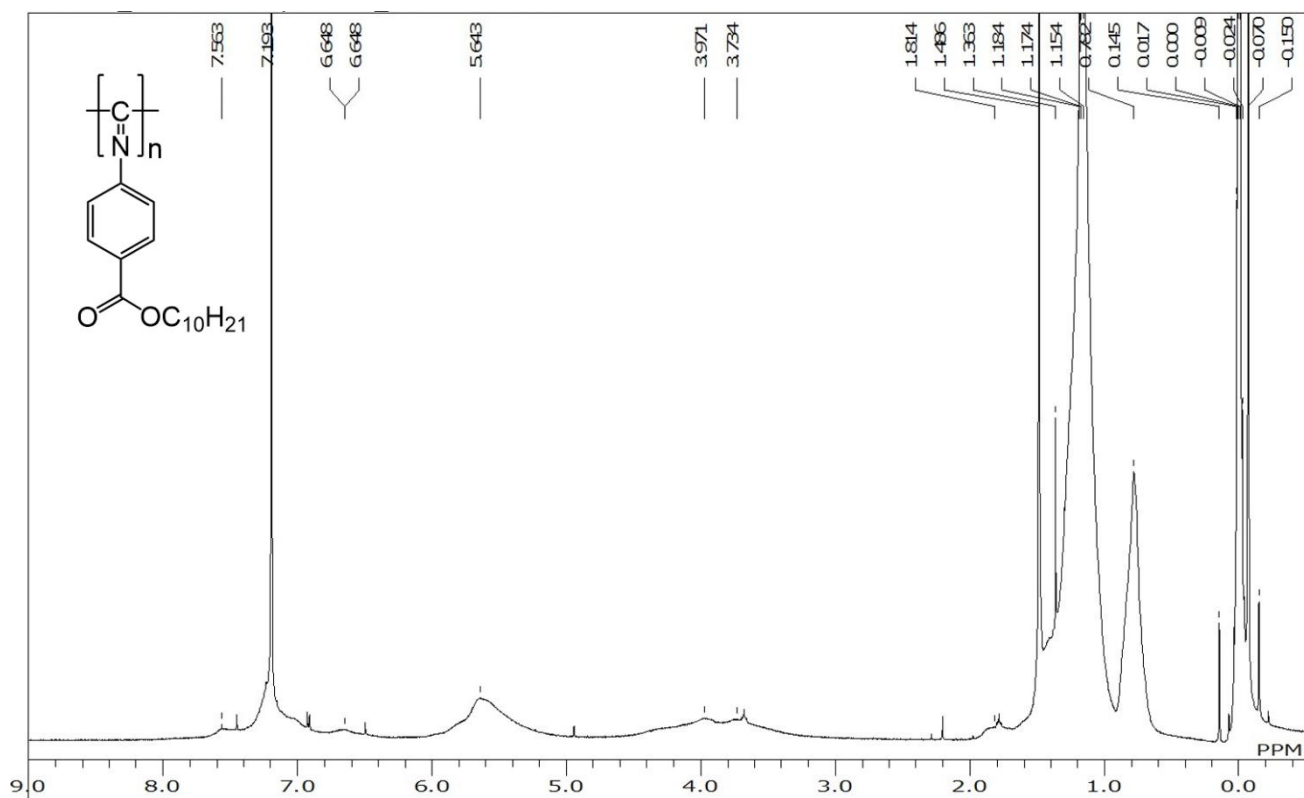
^1H NMR of poly6 (400Hz, CDCl_3).



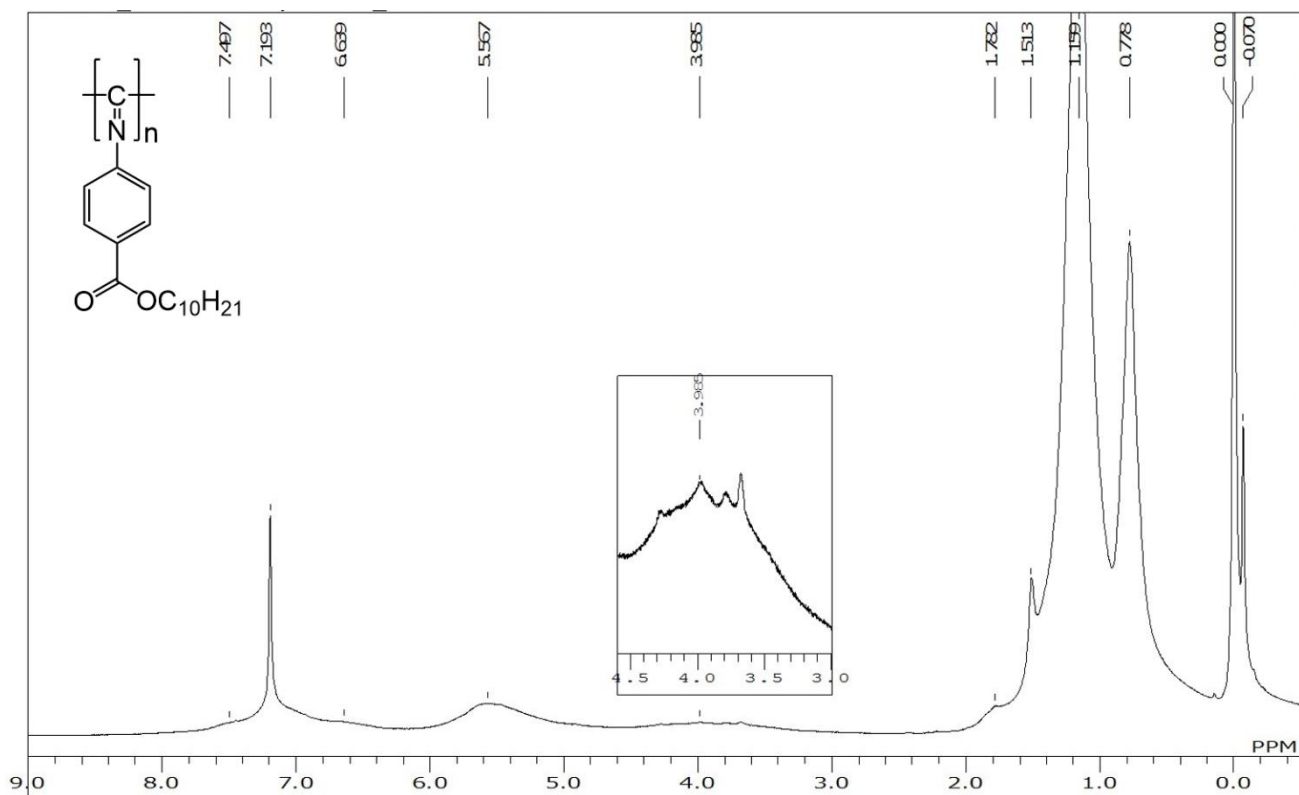
$^1\text{H NMR}$ of poly7 (400Hz, CDCl_3).



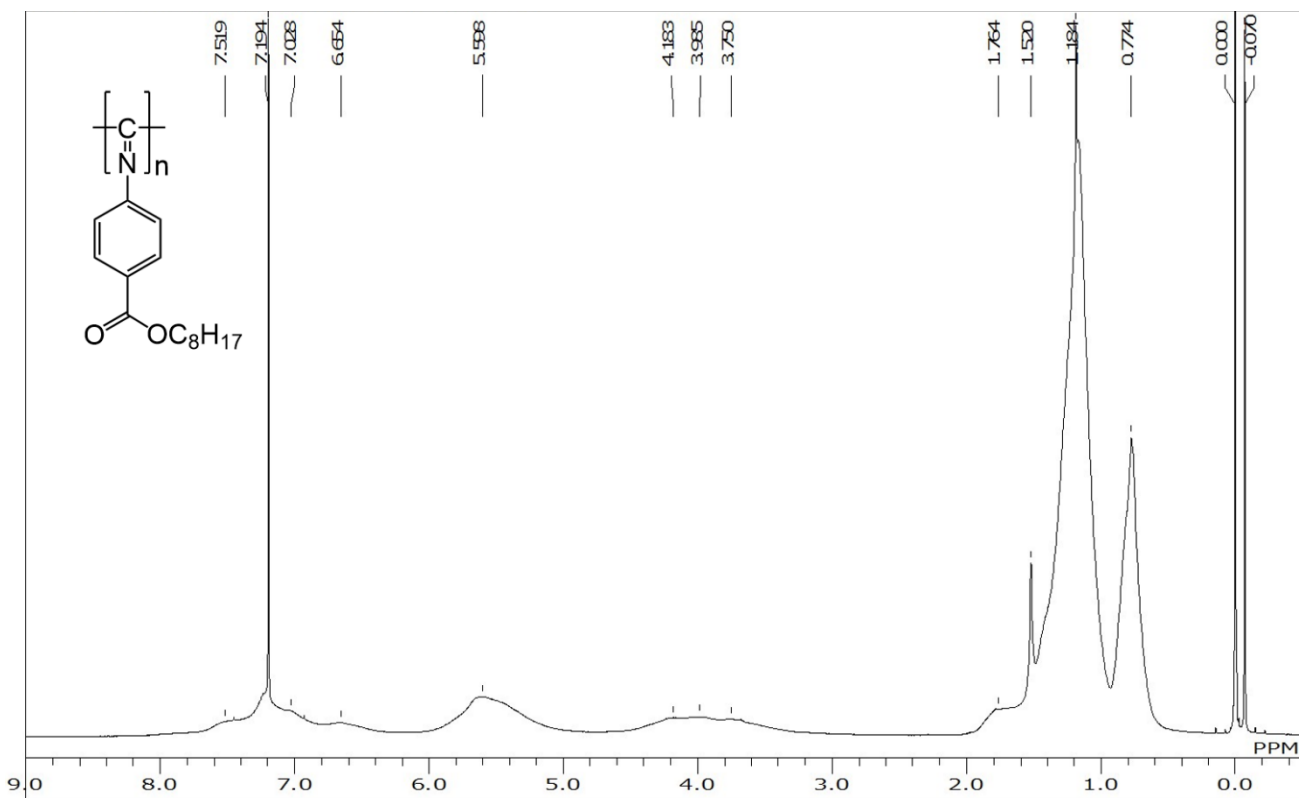
$^1\text{H NMR}$ of poly8 (entry 26) prepared by Pd complex (400Hz, CDCl_3).



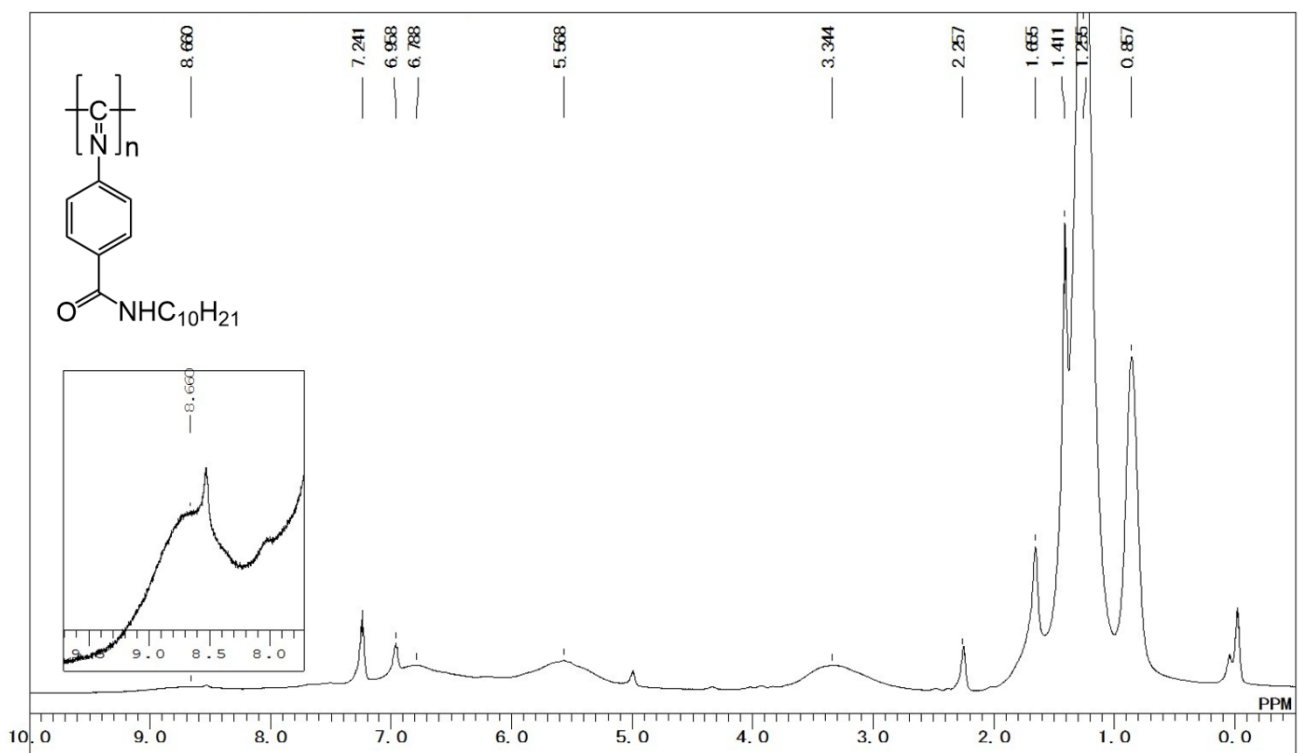
^1H NMR of **poly8** (entry 8) prepared by $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (400Hz, CDCl_3).



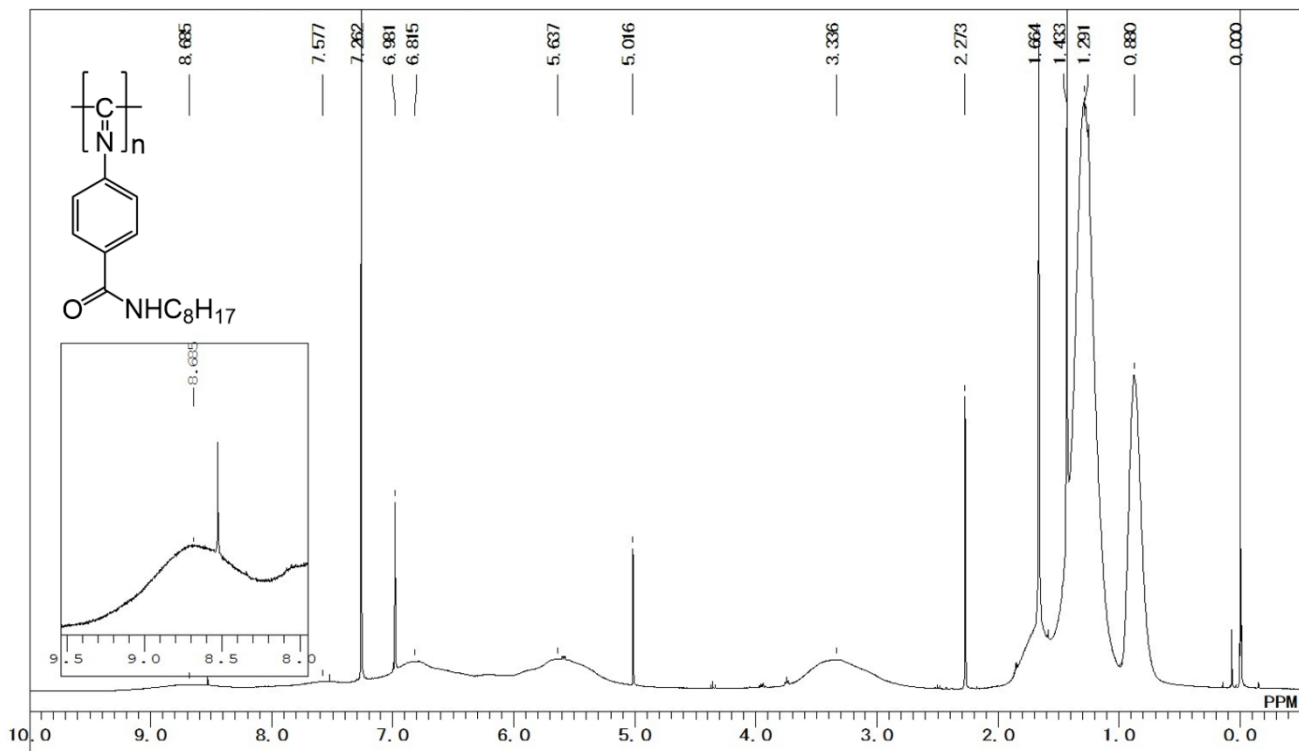
^1H NMR of **poly8** (entry 9) prepared by NiCl_2 (400Hz, CDCl_3).



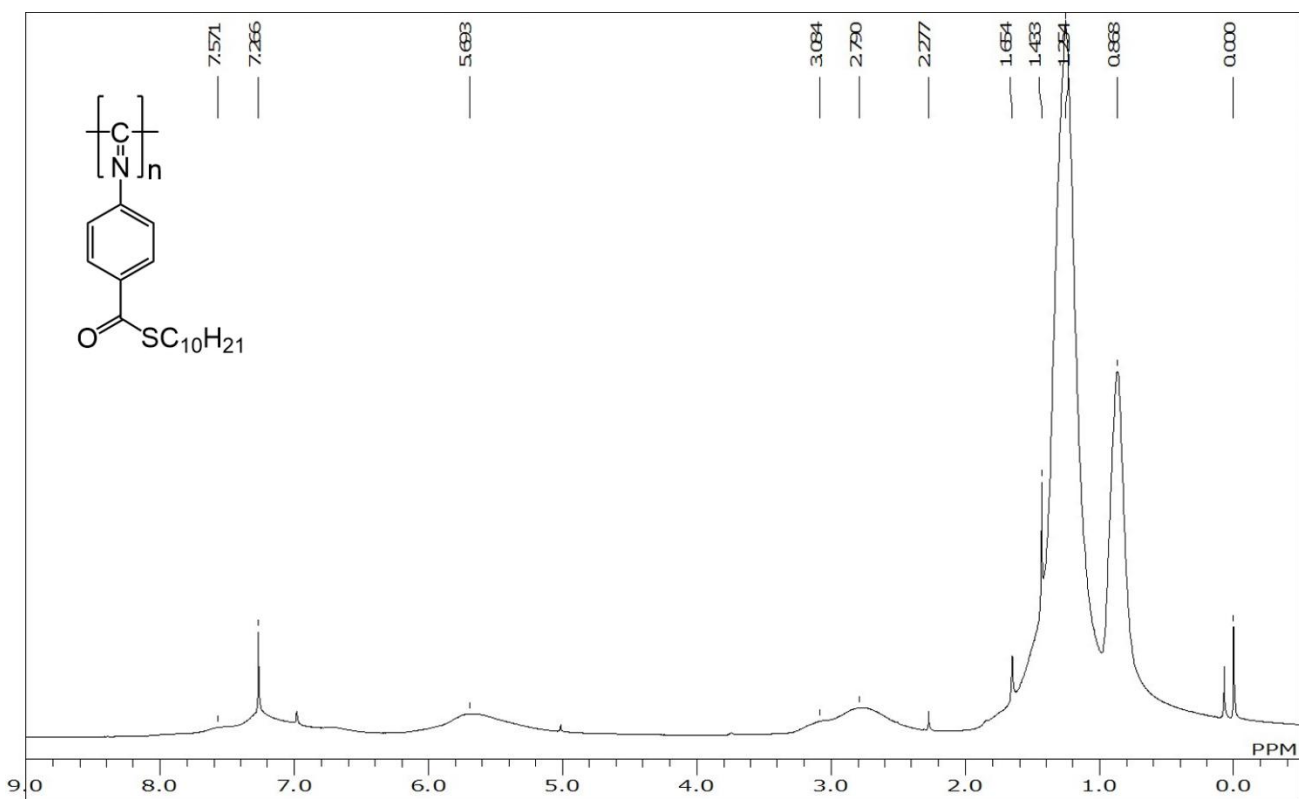
^1H NMR of poly9 (400Hz, CDCl_3).



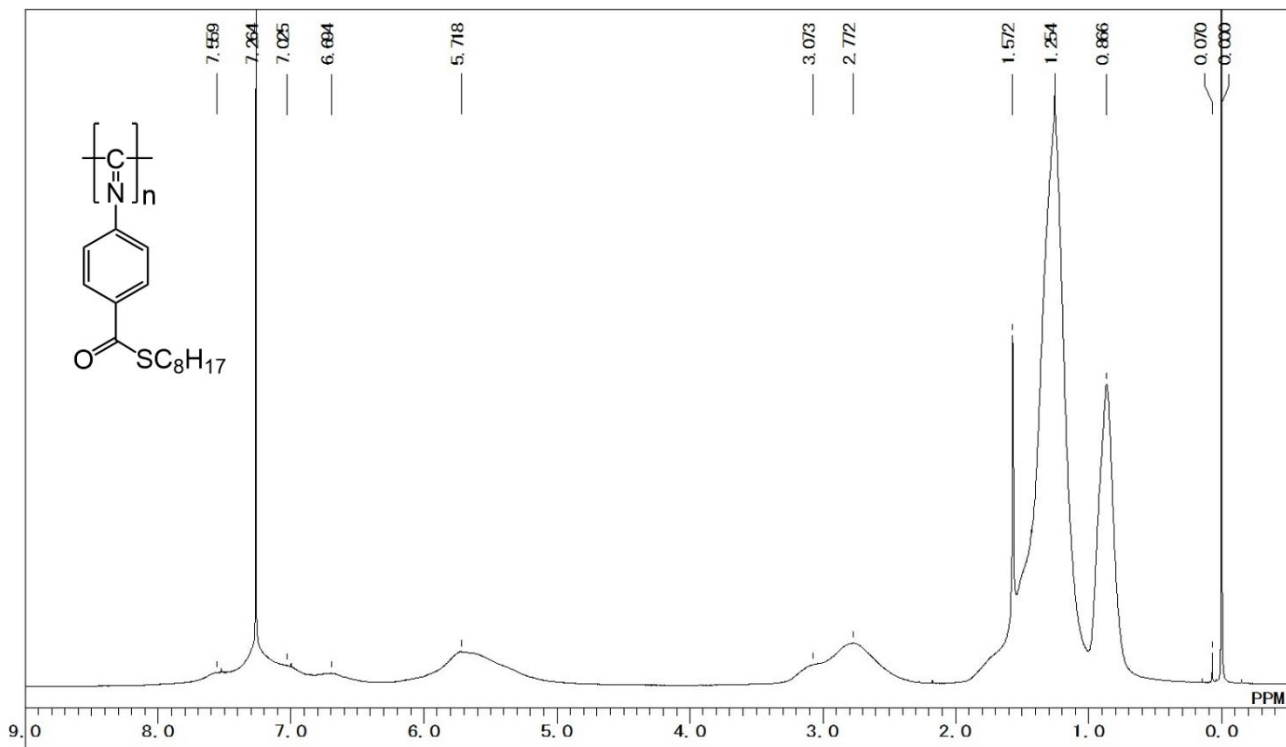
^1H NMR of poly10 (400Hz, CDCl_3).



$^1\text{H NMR}$ of poly11 (400Hz, CDCl_3).



$^1\text{H NMR}$ of poly12 (400Hz, CDCl_3).



¹H NMR of poly13 (400Hz, CDCl₃).