

Supporting Information

Liquid Crystallinity-Enforced Chirality Transfer from Chiral Monosubstituted Polyacetylene Copolymer to Poly(*para*-phenylene ethynylene)

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1. Experimental Methods

1.1 Materials

The chemical reagents we purchased from commercially available sources and were used as received. 18-Crown-6-ether, bicyclo[2.2.1](hepta-2,5-diene)chlororhodium(I) dimer ($[\text{Rh}(\text{nbd})\text{Cl}]_2$) *trans*-dichlorobis(triphenylphosphine)-palladium(II) $[\text{PdCl}_2(\text{TPP})_2]$, and 2,5-diiodobenzoic acid were purchased from Aldrich Co. Ltd. Diisopropylazodicarboxylate (DIAD), *n*-undecanoic acid, 4-pentyn-1-ol, (*R*)-(+)-3-butyn-2-ol, (*S*)-(–)-3-butyn-2-ol, 6-bromo-1-hexanol, trimethylsilylacetylene, and 4'-hydroxy-4-cyano-biphenyl were purchased from Tokyo Kasei Co. Ltd. *Para-trans*-4-*n*-pentyl(cyclohexyl)phenol and copper(I) iodide (CuI) were purchased from Kanto Chemical Co. Ltd. Triphenylphosphine (TPP) was purchased from Wako Co. Ltd. 4-dimethylaminopyridine (DMAP), *N,N'*-dicyclohexylcarboimide (DCC), sodium sulfate (Na_2SO_4), calcium chloride (CaCl_2), potassium carbonate (K_2CO_3), triethyl amine (Et_3N), tetra-*n*-butylammonium fluoride (TBAF), glacial acetic acid, tetrahydrofuran (THF), methanol (MeOH), acetone, ethyl acetate, hexane, chloroform (CHCl_3), and dichloromethane (CH_2Cl_2) were purchased from Nacalai Tesque Co. Ltd. All experiments were performed under argon (>99.9995 % purity) atmosphere. THF, Et_3N , and toluene used were distilled from sodium as a drying agent under argon gas before use. CH_2Cl_2 was distilled from CaCl_2 as a drying agent under argon gas before use.

1.2 Methods

Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-*d* using either JEOL JNM EX400 400 MHz or Bruker AVANCE-600 600 MHz NMR spectrometer. Chemical shifts are represented in parts per million downfield from *tetra*-methylsilane (TMS) as an internal standard. Elemental analysis was measured using a Perkin-Elmer 2400 CHN Elemental Analyzer.

The microscope observation was carried out under crossed nicols using a Nikon ECLIPSE E400 POL POM equipped with a Nikon COOLPIX 950 digital camera and a Linkam TH600PM and L600 heating and cooling stage with temperature control. The samples for observations with POM were

sandwiched between two cover glasses. The LC temperature measurements were done at a heating and cooling rate of 5 °C/min.

Optical absorption spectra were measured using a Hitachi U-3500 spectrometer with quartz cell (for solution) and quartz plate (for cast film). Circular dichroism spectra were measured using JASCO J-820 spectropolarimeter. CHCl₃ solutions of the *mono*-**PA**s were prepared at a concentration of $c = 1.2 \times 10^{-4}$ M. Annealed cast films were prepared by annealing the *mono*-**PA**s at their LC temperature for an hour before spectroscopic measurements were done.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a PLgel 5 μ m MIXED-D (Polymer Laboratories), a JASCO MD915 UV detector and THF as an eluent at a flow rate of 1.0 mL/min during measurements, where the instrument was calibrated using polystyrene (PS) standard, and were calculated on an 807-IT integrator.

XRD diffraction (XRD) measurements of the polymers were performed with a Rigaku ultra X18 diffractometer (X-ray CuK α radiation: 40 kV/300 mA, $\lambda = 0.154$ nm; camera length: 100 mm). XRD patterns were recorded with an X-ray generator with Nickel filtered CuK α radiation and a flat plate camera (RINT2500, Rigaku). The polymers were heated up to isotropic state, and then slowly cooled to room temperature via LC states, yielding free standing LC film samples. The LC films were mounted on the XRD sample holder and the diffraction pattern was recorded on an imaging plate and scanned by a R-Axis DS3A imaging plate reader at 100 μ m resolution. XRD patterns were evaluated using Rigaku RINT 2100 data evaluation software.

1.3 Syntheses of Monomers and Polymers

The syntheses of the *mono*-**PA** monomers: **M1** and (*R*)-/(*S*)-**M2**, **LC-PPE** precursors: (**1**), (**2**), (**3**), and the polymers **PA1**, (*R*)-/(*S*)-**PA**_{0.75-0.25*}, (*R*)-/(*S*)-**PA**_{0.50-0.50*}, (*R*)-/(*S*)-**PA**_{0.25-0.75*}, (*R*)-/(*S*)-**PA2**, and **LC-PPE** are written below.

1-(pent-4-yn-1-yloxy)-4-(4-pentylcyclohexyl)benzene (M1)

1-(pent-4-yn-1-yloxy)-4-(4-pentylcyclohexyl)benzene (**M1**) was synthesized as follows. Into a 300 mL three-necked flask were added TPP (6.24 g, 24 mmol) and *para-trans*-4-*n*-

pentyl(cyclohexyl) phenol (5.32 g, 22 mmol) under argon gas and dissolved in THF (70 mL). In the addition funnel, a mixture of DIAD (12.02 g, 40 wt. % in toluene, 24 mmol), 4-pentyn-1-ol (2.00 g, 44 mmol) and 30 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. Thin layer chromatography (TLC) indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 \times). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The product was recrystallized from MeOH and dried in vacuo to give 4.43 g (15 mmol) of **M1** as a white crystal. Yield = 66%.

Anal. Chemical Formula: $(\text{C}_{22}\text{H}_{32}\text{O})_n$ (312.49) $_n$: Calcd. C, 84.56; H, 10.32; O, 5.12. Found C, 84.66; H, 10.35. ^1H NMR (400 MHz, CDCl_3): δ = 0.89 (t, 3H, J = 7.2 Hz, $-\text{Ar}-\text{C}_6\text{H}_{10}-(\text{CH}_2)_4\text{CH}_3$), 0.93–2.02 (m, 19H, $-\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}\equiv\text{C}-$, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}-(\text{CH}_2)_4\text{CH}_3$), 2.38–2.44 (m, 3H, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}_2-\text{C}_5\text{H}_{11}$, and $-\text{Ar}-\text{O}-(\text{CH}_2)_2\text{CH}_2-\text{C}\equiv\text{C}-$), 2.82 (s, 1H, $-\text{C}\equiv\text{CH}$), 4.04 (t, 2H, J = 6.4 Hz, $-\text{Ar}-\text{O}-\text{CH}_2(\text{CH}_2)_2-\text{C}\equiv\text{C}-$), 6.83 (d, 2H, J = 8.4 Hz, Ar-H *ortho* to $-\text{O}-(\text{CH}_2)_3-\text{C}\equiv\text{C}-$), 7.12 (d, 2H, J = 8.8 Hz, Ar-H *meta* to $-\text{O}-(\text{CH}_2)_3-\text{C}\equiv\text{C}-$). ^{13}C NMR (100 MHz, CDCl_3): δ = 14.0, 15.2, 22.6, 33.6, 34.6, 37.3, 43.7, 66.3, 68.6, 114.2, 127.5, 140.1, 156.7

(R)-1-methylpropargyl-undecanoate ((R)-M2)

(R)-1-methylpropargyl-undecanoate ((R)-M2) was synthesized as follows. *n*-undecanoic acid (3.19 g, 17 mmol), *(R)*-(+)-3-butyn-2-ol (1.00 g, 15 mmol), DCC (3.53 g, 17 mmol) and DMAP (2.10 g, 17 mmol) were added under argon gas into a 200 mL round bottom flask, dissolved in CH_2Cl_2 (70 mL) and then stirred. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 \times). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give **(R)-M2** (2.91 g, 12 mmol) as a clear liquid. Yield = 86%.

Anal. Chemical Formula: $(C_{15}H_{26}O_2)_n$ (238.37) $_n$: Calcd. C, 75.58; H, 10.99; O, 13.42. Found C, 75.83; H, 11.10. 1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, 3H, J = 8.0 Hz, $-OCO-(CH_2)_9CH_3$), 1.23–1.67 (m, 19H, $-OCO-CH_2(CH_2)_8CH_3$, and $-C\equiv C-CH(CH_3)OCO-$), 2.23–2.37 (m, 2H, $-OCO-CH_2(CH_2)_8CH_3$), 2.44 (s, 1H, $-C\equiv CH$), 5.41–5.48 (m, 1H, $-C\equiv C-CH(CH_3)OCO-$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.2, 22.7, 24.8, 29.0, 29.2, 29.4, 31.9, 34.2, 59.7, 72.6, 76.7, 77.0, 77.3, 82.2, 172.4.

(S)-1-methylpropargyl-undecanoate ((S)-M2)

(S)-1-methylpropargyl-undecanoate ((S)-M2) was synthesized as follows. Into a 200 mL round bottom flask were added *n*-undecanoic acid (3.19 g, 17 mmol), (S)-(-)-3-butyn-2-ol (1.00 g, 15 mmol), DCC (3.53 g, 17 mmol) and DMAP (2.10 g, 17 mmol) were added under argon gas, dissolved in CH_2Cl_2 (70 mL) and then stirred. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with $CHCl_3$ (3 \times). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using $CHCl_3$ as eluent. The collected liquid was evaporated and dried under vacuum to give (S)-M2 (3.29 g, 13 mmol) as a clear liquid. Yield = 97%.

Anal. Chemical Formula: $(C_{15}H_{26}O_2)_n$ (238.37) $_n$: Calcd. C, 75.58; H, 10.99; O, 13.42. Found C 75.35, H 10.97. 1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 3H, J = 7.2 Hz, $-OCO-(CH_2)_9CH_3$), 1.22–1.67 (m, 19H, $-OCO-CH_2(CH_2)_8CH_3$, and $-C\equiv C-CH(CH_3)OCO-$), 2.27–2.37 (m, 2H, $-OCO-CH_2(CH_2)_8CH_3$), 2.44 (s, 1H, $-C\equiv CH$), 5.38–5.49 (m, 1H, $-C\equiv C-CH(CH_3)OCO-$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.2, 22.7, 24.9, 29.0, 29.3, 29.5, 31.9, 34.2, 59.7, 72.6, 76.7, 77.0, 77.3, 82.2, 172.4.

Liquid Crystalline *mono*-PA1 (PA1)

PA1 was synthesized as follows. Et_3N (1 mL) and $[Rh(nbd)Cl]_2$ (21 mg, 0.05 mmol) was added under argon into a Schlenk flask. The catalyst mixture was stirred at room temperature for 30 min, and then M1 (1.41 g, 4.52 mmol) was dissolved in 1 mL THF and was then added to the reaction mixture. The reaction mixture was stirred for 24 h. The mixture was added dropwise to 800 mL of

MeOH under stirring. The polymer precipitate stirred for 24 h, which was then filtered, washed with MeOH and dried in a vacuum oven. A brownish white powder was obtained with a yield of 38% (0.54 g, 1.72 mmol). M_w . 30,000 M_w/M_n . 1.5 (GPC, PS calibration).

Anal. $(C_{22}H_{32}O)_n$ (312.49) $_n$: Calcd. C, 84.56; H, 10.32; O, 5.12. Found C 82.33, H 10.09. 1H NMR (400 MHz, $CDCl_3$): δ = 0.88–1.10 (br, 5H, $-Ar-C_6H_{10}-(CH_2)_3CH_2CH_3$), 1.11–2.10 (br, 17H, $-Ar-O-CH_2CH_2CH_2-C=C-$, $-O-Ar-CH(CH_2)_4CH-(CH_2)_3CH_2CH_3$), 2.18–2.60 (br, 3H, $-O-Ar-CH(CH_2)_4CH_2-C_5H_{11}$, and $-Ar-O-(CH_2)_2CH_2-C=C-$), 3.55–3.90 (br, 2H, $-Ar-O-CH_2(CH_2)_2-C=C-$), 5.97 (br, 0.5H, $-C=CH$ *cis*), 6.50–7.15 (br, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.8, 33.7, 34.6, 37.3, 43.5, 114.1, 127.3.

(R)-PA_{0.75-0.25}*

(R)-PA_{0.75-0.25}* was synthesized as follows. Into a Schlenk flask, Et_3N (1 mL) and $[Rh(nbd)Cl]_2$ (10 mg, 0.02 mmol) was stirred at room temperature for 30 min under argon. **M1** (0.53 g, 1.69 mmol) and **(R)-M2** (0.13 g, 0.56 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise into the reaction flask. The reaction mixture was stirred for 24 h. The resultant solution was then added dropwise to 800 mL of MeOH under stirring. The precipitate was allowed to stand overnight, which was then filtered. The polymer was washed with MeOH and dried in a vacuum oven to a constant weight. A light brown powder was obtained with a yield of 49% (0.32 g, 1.08 mmol). M_w . 45,000 M_w/M_n . 1.6 (GPC, PS calibration).

Anal. $(C_{20.25}H_{30.50}O_{1.25})_n$ (294.10) $_n$: Calcd. C, 82.72; H, 10.48; O, 6.80. Found C 80.75, H 10.35. 1H NMR (400 MHz, $CDCl_3$): δ = 0.80–1.1 (br, 4.80H, $-Ar-C_6H_{10}-(CH_2)_4CH_3$, and $-OCO-(CH_2)_9CH_3$), 1.12–1.78 (br, 19H, $-Ar-O-CH_2CH_2CH_2-C=C-$, $-O-Ar-CH(CH_2)_4CH-(CH_2)_4CH_3$, $-OCO-CH_2(CH_2)_8CH_3$, and $-C=C-CH(CH_3)OCO-$), 1.79–1.98 (br, 4.3H, $-O-Ar-CH(CH_2)_4CH_2-C_5H_{11}$, $-Ar-O-(CH_2)_2CH_2-C=C-$, and $-OCO-CH_2(CH_2)_8CH_3$), 3.47–4.10 (br, 2H, $-Ar-O-CH_2(CH_2)_2-C=C-$), 5.99 (br, 0.3H, $-C=CH$ *cis*), 6.27 (br, 0.15H, $-C=CH$ *trans*), 6.54–7.19 (br, 3H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 19.3, 22.7, 33.7, 34.6, 37.5, 47.1, 53.8, 59.1, 86.5, 131.6, 136.4, 136.9, 152.7, 158.4, 170.3.

(S)-PA_{0.75-0.25}*

(S)-PA_{0.75-0.25}* was synthesized as follows. Et₃N (1 mL) and [Rh(nbd)Cl]₂ (5 mg, 0.01 mmol) was added under argon into a Schlenk flask. The catalyst mixture was stirred at room temperature for 30 min. **M1** (0.26 g, 0.85 mmol) and **(S)-M2** (0.07 g, 0.28 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise to the reaction mixture. The reaction mixture was stirred for 24 h. The mixture was added dropwise to 800 mL of MeOH under stirring. The polymer precipitate stirred for 24 h, which was then filtered, washed with MeOH and dried in a vacuum oven. A dark light brown powder was obtained with a yield of 46% (0.15 g, 0.52 mmol). *M_w*. 42,000 *M_w/M_n*. 2.7 (GPC, PS calibration).

Anal. (C_{20.25}H_{30.50}O_{1.25})_n (294.10)_n: Calcd. C, 82.72; H, 10.48; O, 6.80. Found C 80.51, H 10.76. ¹H NMR (400 MHz, CDCl₃): δ = 0.80–1.07 (br, 5.70H, –Ar–C₆H₁₀–(CH₂)₄CH₃, and –OCO–(CH₂)₉CH₃), 1.12–1.64 (br, 19H, –Ar–O–CH₂CH₂CH₂–C=C–, –O–Ar–CH(CH₂)₄CH–(CH₂)₄CH₃, –OCO–CH₂(CH₂)₈CH₃, and –C=C–CH(CH₃)OCO–), 1.79–2.01 (br, 4.5H, –O–Ar–CH(CH₂)₄CH₂–C₅H₁₁, –Ar–O–(CH₂)₂CH₂–C=C–, and –OCO–CH₂(CH₂)₈CH₃), 3.48–3.97 (br, 3.3H, –Ar–O–CH₂(CH₂)₂–C=C–), 5.99 (br, 0.4H, –C=CH *cis*), 6.27 (br, 0.1H, –C=CH *trans*), 6.50–7.15 (br, 3H, Ar–H). ¹³C NMR (100 MHz, CDCl₃): δ = 14.1, 22.7, 25.0, 26.9, 29.7, 33.7, 34.6, 37.4, 37.5, 40.6, 43.7, 52.3, 60.0, 66.2, 70.7, 114.1, 123.1, 127.3, 152.5.

(R)-PA_{0.50-0.50}*

(R)-PA_{0.50-0.50}* was synthesized as follows. Into a Schlenk flask, Et₃N (1 mL) and [Rh(nbd)Cl]₂ (10 mg, 0.02 mmol) was stirred at room temperature for 30 min under argon. **M1** (0.35 g, 1.13 mmol) and **(R)-M2** (0.27 g, 1.13 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise into the reaction flask. The reaction mixture was stirred for 24 h. The resultant solution was then added dropwise to 800 mL of MeOH under stirring. The precipitate was allowed to stand overnight, which was then filtered. The polymer was washed with MeOH and dried in a vacuum oven to a constant weight. A brown powder was obtained with a yield of 71% (0.44 g, 1.60 mmol). *M_w*. 44,000 *M_w/M_n*. 1.6 (GPC, PS calibration).

Anal. (C_{18.50}H₂₉O_{1.50})_n (275.48)_n: Calcd. C, 80.66; H, 10.63; O, 8.71. Found C 78.60, H 10.48. ¹H NMR (400 MHz, CDCl₃): δ = 0.78–1.06 (br, 5H, –Ar–C₆H₁₀–(CH₂)₃CH₂CH₃, –OCO–(CH₂)₉CH₃),

1.08–1.55 (br, 19H, $-\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}=\text{C}-$, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}-(\text{CH}_2)_3\text{CH}_2\text{CH}_3$, $-\text{OCO}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$, and $-\text{C}=\text{C}-\text{CH}(\text{CH}_3)\text{OCO}-$), 1.69–1.91 (br, 2.8H, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}_2-\text{C}_5\text{H}_{11}$, and $-\text{Ar}-\text{O}-(\text{CH}_2)_2\text{CH}_2-\text{C}=\text{C}-$), 2.12–2.56 (br, 2H, $-\text{OCO}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$), 3.61–4.04 (br, 1H, $-\text{Ar}-\text{O}-\text{CH}_2(\text{CH}_2)_2-\text{C}=\text{C}-$), 5.30–5.99 (br, 0.01H, $-\text{C}=\text{CH}$ *cis*), 6.01–6.44 (br, 0.4H, $-\text{C}=\text{CH}$ *trans*), 6.63–7.15 (br, 2H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 22.7, 25.1, 26.8, 29.4, 29.7, 32.0, 33.7, 34.6, 37.4, 97.2, 114.1, 127.5, 140.9, 146.5, 151.5, 175.4.

(S)-PA_{0.50-0.50}*

(S)-PA_{0.50-0.50}* was synthesized as follows. Et_3N (1 mL) and $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (5 mg, 0.01 mmol) was added under argon into a Schlenk flask. The catalyst mixture was stirred at room temperature for 30 min. **M1** (0.18 g, 0.56 mmol) and **(S)-M2** (0.13 g, 0.56 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise to the reaction mixture. The reaction mixture was stirred for 24 h. The mixture was added dropwise to 800 mL of MeOH under stirring. The polymer precipitate stirred for 24 h, which was then filtered, washed with MeOH and dried in a vacuum oven. A brown powder was obtained with a yield of 66% (0.21 g, 0.75 mmol). M_w . 70,000 M_w/M_n . 2.9 (GPC, PS calibration).

Anal. $(\text{C}_{18.50}\text{H}_{29}\text{O}_{1.50})_n$ (275.48) $_n$: Calcd. C, 80.66; H, 10.63; O, 8.71. Found C 78.83, H 10.53. ^1H NMR (400 MHz, CDCl_3): δ = 0.81–1.07 (br, 5H, $-\text{Ar}-\text{C}_6\text{H}_{10}-(\text{CH}_2)_3\text{CH}_2\text{CH}_3$, $-\text{OCO}-(\text{CH}_2)_9\text{CH}_3$), 1.08–1.64 (br, 21H, $-\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}=\text{C}-$, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}-(\text{CH}_2)_3\text{CH}_2\text{CH}_3$, $-\text{OCO}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$, and $-\text{C}=\text{C}-\text{CH}(\text{CH}_3)\text{OCO}-$), 1.43–1.70 (br, 2.8H, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}_2-\text{C}_5\text{H}_{11}$, and $-\text{Ar}-\text{O}-(\text{CH}_2)_2\text{CH}_2-\text{C}=\text{C}-$), 2.05–2.56 (br, 2.4H, $-\text{OCO}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$), 3.55–3.96 (br, 1H, $-\text{Ar}-\text{O}-\text{CH}_2(\text{CH}_2)_2-\text{C}=\text{C}-$), 5.30–5.97 (br, 0.3H, $-\text{C}=\text{CH}$ *cis*), 6.19–6.41 (br, 0.7H, $-\text{C}=\text{CH}$ *trans*), 6.63–7.10 (br, 2H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 22.7, 26.7, 29.4, 29.7, 31.9, 32.3, 33.7, 34.6, 37.3, 48.9, 60.6, 69.1, 72.1, 114.1, 127.4, 137.2, 144.9, 151.1.

(R)-PA_{0.25-0.75}*

(R)-PA_{0.25-0.75}* was synthesized as follows. Into a Schlenk flask, Et₃N (1 mL) and [Rh(nbd)Cl]₂ (10 mg, 0.02 mmol) was stirred at room temperature for 30 min under argon. **M1** (0.18 g, 0.56 mmol) and **(R)-M2** (0.40 g, 1.69 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise into the reaction flask. The reaction mixture was stirred for 24 h. The resultant solution was then added dropwise to 800 mL of MeOH under stirring. The precipitate was allowed to stand overnight, which was then filtered. The polymer was washed with MeOH and dried in a vacuum oven to a constant weight. A brown powder was obtained with a yield of 77% (0.44 g, 1.73 mmol). *M_w*. 81,000 *M_w/M_n*. 2.8 (GPC, PS calibration).

Anal. (C_{16.75}H_{27.50}O_{1.75})_n (256.94)_n: Calcd. C, 78.29; H, 10.81; O, 10.90. Found C 77.01, H 10.81. ¹H NMR (400 MHz, CDCl₃): δ = 0.78–0.94 (br, 6.4H, –Ar–C₆H₁₀–(CH₂)₃CH₂CH₃, –OCO–(CH₂)₉CH₃), 1.08–1.69 (br, 29H, –Ar–O–CH₂CH₂CH₂–C=C–, –O–Ar–CH(CH₂)₄CH–(CH₂)₃CH₂CH₃, –OCO–CH₂(CH₂)₈CH₃, and –C=C–CH(CH₃)OCO–), 1.82–2.11 (br, 2H, –OCO–CH₂(CH₂)₈CH₃), 2.27–2.41 (br, 3H, –O–Ar–CH(CH₂)₄CH₂–C₅H₁₁, and –Ar–O–(CH₂)₂CH₂–C=C–), 3.69–3.99 (br, 0.6H, –Ar–O–CH₂(CH₂)₂–C=C–), 5.30–5.99 (br, 0.9H, –C=CH *cis*), 6.02–6.52 (br, 1.1H, –C=CH *trans*), 6.63–7.03 (br, 1.5H, Ar–H). ¹³C NMR (100 MHz, CDCl₃): δ = 14.1, 22.7, 25.0, 26.7, 29.4, 29.7, 31.9, 32.2, 33.7, 34.4, 34.6, 37.4, 43.7, 52.4, 114.1, 127.3, 140.8, 171.9.

(S)-PA_{0.25-0.75}*

(S)-PA_{0.25-0.75}* was synthesized as follows. Et₃N (1 mL) and [Rh(nbd)Cl]₂ (5 mg, 0.01 mmol) was added under argon into a Schlenk flask. The catalyst mixture was stirred at room temperature for 30 min. **M1** (0.09 g, 0.28 mmol) and **(S)-M2** (0.20 g, 0.85 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise to the reaction mixture. The reaction mixture was stirred for 24 h. The mixture was added dropwise to 800 mL of MeOH under stirring. The polymer precipitate stirred for 24 h, which was then filtered, washed with MeOH and dried in a vacuum oven. A brown powder was obtained with a yield of 80% (0.23 g, 0.90 mmol). *M_w*. 102,000 *M_w/M_n*. 2.2 (GPC, PS calibration).

Anal. (C_{16.75}H_{27.50}O_{1.75})_n (256.94)_n: Calcd. C, 78.29; H, 10.81; O, 10.90. Found C 76.07, H 10.55.

¹H NMR (400 MHz, CDCl₃): δ = 0.78–0.94 (br, 5.3H, –Ar–C₆H₁₀–(CH₂)₃CH₂CH₃, –OCO–(CH₂)₉CH₃), 1.25–1.63 (br, 26H, –Ar–O–CH₂CH₂CH₂–C=C–, –O–Ar–CH(CH₂)₄CH–(CH₂)₃CH₂CH₃, –OCO–CH₂(CH₂)₈CH₃, and –C=C–CH(CH₃)OCO–), 1.82–1.92 (br, 2H, –OCO–CH₂(CH₂)₈CH₃), 2.09–2.41 (br, 3H, –O–Ar–CH(CH₂)₄CH₂–C₅H₁₁, and –Ar–O–(CH₂)₂CH₂–C=C–), 3.66–4.03 (br, 1H, –Ar–O–CH₂(CH₂)₂–C=C–), 5.41–5.82 (br, 1.3H, –C=CH *cis*), 5.97–6.49 (br, 1.6H, –C=CH *trans*), 6.67–7.12 (br, 1.5H, Ar–H). ¹³C NMR (100 MHz, CDCl₃): δ = 14.1, 18.9, 22.7, 29.4, 29.7, 30.9, 32.0, 37.7, 114.0, 127.6, 155.2, 164.7, 173.6.

(R)-PA2

(R)-PA2 was synthesized as follows. Into a Schlenk flask, Et₃N (1 mL) and [Rh(nbd)Cl]₂ (10 mg, 0.02 mmol) was stirred at room temperature for 30 min under argon, and then **(R)-M2** (0.54 g, 2.26 mmol) dissolved in 1 mL THF was added to it. The reaction mixture was stirred for 24 h. The resultant solution was then added dropwise to 800 mL of MeOH under stirring. The precipitate was allowed to stand overnight, which was then filtered. The polymer was washed with MeOH and dried in a vacuum oven to a constant weight. A dark amber colored viscous liquid was obtained with a yield of 74% (0.39 g, 1.67 mmol). *M*_w. 93,000 *M*_w/*M*_n. 3.4 (GPC, PS calibration).

Anal. (C₁₅H₂₆O₂)_n (238.37)_n: Calcd. C, 75.58; H, 10.99; O, 13.42. Found C 75.43, H 10.81. ¹H NMR (400 MHz, CDCl₃): δ = 0.80–0.98 (br, 3H, –OCO–(CH₂)₉CH₃), 1.01–1.69 (br, 19H, –OCO–CH₂(CH₂)₈CH₃, and –C=C–CH(CH₃)OCO–), 2.17–2.40 (br, 2H, –OCO–CH₂(CH₂)₈CH₃), 5.50–5.70 (br, 0.75H, –C=C–CH(CH₃)OCO–), 6.61 (br, 0.75H, –C=CH *trans*). ¹³C NMR (100 MHz, CDCl₃): δ = 14.1, 22.7, 25.0, 29.3, 29.4, 29.5, 29.6, 29.7, 30.9, 31.9, 34.4, 52.4, 71.3, 122.8, 141.0, 171.9.

(S)-PA2

(S)-PA2 was synthesized as follows. Et₃N (1 mL) and [Rh(nbd)Cl]₂ (5 mg, 0.01 mmol) was added under argon into a Schlenk flask. The catalyst mixture was stirred at room temperature for 30 min, and then **(S)-M2** (0.27 g, 1.13 mmol) was dissolved in 1 mL THF and was then added to the reaction mixture. The reaction mixture was stirred for 24 h. The mixture was added dropwise to

800 mL of MeOH under stirring. The polymer precipitate stirred for 24 h, which was then filtered, washed with MeOH and dried in a vacuum oven. A dark amber colored viscous liquid was obtained with a yield of 84% (0.23 g, 0.94 mmol). M_w . 100,000 M_w/M_n . 3.0 (GPC, PS calibration).

Anal. $(C_{15}H_{26}O_2)_n$ (238.37) $_n$: Calcd. C, 75.58; H, 10.99; O, 13.42. Found C 74.55, H 10.90. 1H NMR (400 MHz, $CDCl_3$): δ = 0.78–0.82 (br, 3H, $-OCO-(CH_2)_9CH_3$), 1.00–1.67 (br, 19H, $-OCO-CH_2(CH_2)_8CH_3$, and $-C=C-CH(CH_3)OCO-$), 2.17–2.40 (br, 2H, $-OCO-CH_2(CH_2)_8CH_3$), 5.50–5.70 (br, 0.8H, $-C=C-CH(CH_3)OCO-$), 6.41 (br, 0.8H, $-C=CH$ *trans*). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 20.4, 22.7, 25.0, 29.3, 29.4, 29.6, 31.9, 34.3, 71.1, 115.9, 122.7, 140.9, 171.9.

4'-((6-hydroxyhexyl)oxy)-[1,1'-biphenyl]-4-cyano (1)

4'-((6-hydroxyhexyl)oxy)-[1,1'-biphenyl]-4-cyano (**1**) was synthesized as follows. Into a 300 mL three necked flask were added 3.59 g (18 mmol) of 4'-hydroxy-4-cyano-biphenyl, 3.8 g of K_2CO_3 (28 mmol) and 100 mL acetone under argon atmosphere. After all the reagents were dissolved, the solution was heated to 60 °C and refluxed under constant stirring. In the addition funnel, a solution of 6-bromo-1-hexanol (4.0 g, 22 mmol) and 20 mL THF was prepared. The THF solution in the addition funnel was added dropwise to the solution in the flask. A catalytic amount of 18-crown-6-ether was then added, the solution was left stirring overnight and then cooled to room temperature, the layers were separated and washed with water and $CHCl_3$ (3 \times). The combined organic layers were dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using ethyl acetate:hexane, 1:1 as eluent. The collected liquid was evaporated and dried under vacuum to give compound (**1**) (3.95 g, 13.4 mmol) as a white powder. Yield = 60%.

Anal. Chemical Formula: $(C_{19}H_{21}NO_2)_n$ (295.38) $_n$: Calcd. C, 77.26; H, 7.17; O, 10.83; N, 4.74. Found C, 77.27; H, 7.21; N, 4.71. 1H NMR (400 MHz, $CDCl_3$): δ = 1.28–1.21, 1.45–1.66, 1.82–1.89 (m, 8H, $HO-CH_2(CH_2)_4CH_2-Ar$), 3.42 (s, 1H, $HO-CH_2(CH_2)_4CH_2-Ar$), 3.69 (t, 2H, J = 5.6 Hz, $HO-CH_2(CH_2)_4CH_2-Ar$), 4.03 (t, 2H, J = 6.5 Hz, $HO-CH_2(CH_2)_4CH_2-Ar$), 6.99–7.02 (m, 2H, $Ar-H$ *ortho* to $HO-CH_2(CH_2)_4CH_2-$), 7.53–7.55 (m, 2H, $Ar-H$ *meta* to $HO-CH_2(CH_2)_4CH_2-$),

7.64–7.72 (m, 4H, Ar–H *ortho* and *meta* to $-\text{C}\equiv\text{N}$). ^{13}C NMR (100 MHz, CDCl_3): δ = 25.9, 26.3, 29.6, 33.1, 63.2, 68.4, 115.4, 127.3, 128.6, 132.8, 145.7, 156.7.

6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl 2,5-diiodobenzoate (2)

6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl 2,5-diiodobenzoate (**2**) was synthesized as follows. 2,5-diiodobenzoic acid (1.20 g, 3.21 mmol), (**1**) (1.14 g, 3.85 mmol), DCC (0.79 g, 3.85 mmol) and DMAP (0.47 g, 3.85 mmol) were added under argon gas into a 200 mL round bottom flask, dissolved in CH_2Cl_2 (60 mL) and then stirred. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 \times). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give (**2**) (1.52 g, 2.34 mmol) as a white powder. Yield = 73%.

Anal. Chemical Formula: $(\text{C}_{26}\text{H}_{23}\text{I}_2\text{NO}_3)_n$ (651.28) $_n$: Calcd. C, 47.95; H, 3.56; O, 7.37; N, 2.15. Found C, 47.81; H, 3.66; N, 2.11. ^1H NMR (400 MHz, CDCl_3): δ = 1.51–1.59, 1.80–1.88 (m, 8H, $\text{HO}-\text{CH}_2(\text{CH}_2)_4\text{CH}_2-\text{Ar}$), 4.03 (t, 2H, J = 6.4 Hz, $\text{HO}-\text{CH}_2(\text{CH}_2)_4\text{CH}_2-\text{Ar}$), 4.36 (t, 2H, J = 6.7 Hz, $\text{HO}-\text{CH}_2(\text{CH}_2)_4\text{CH}_2-\text{Ar}$), 6.99 (d, 2H, J = 9.0 Hz, Ar–H *ortho* and *para* to $-\text{COO}(\text{CH}_2)_6-\text{Ar}$), 7.43–7.53 (m, 4H, Ar–H *ortho* and *meta* to $-\text{COO}-(\text{CH}_2)_6\text{O}-$), 7.63–7.70 (m, 4H, Ar–H *ortho* and *meta* to $-\text{C}\equiv\text{N}$), 8.06 (m, 1H, Ar–H *meta* to $-\text{COO}(\text{CH}_2)_6-\text{Ar}$). ^{13}C NMR (100 MHz, CDCl_3): δ = 21.4, 23.5, 25.6, 32.0, 62.9, 67.5, 97.9, 99.1, 110.9, 115.1, 127.0, 132.5, 139.8, 142.6, 149.7, 155.8, 164.4.

6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl 2,5-diethynylbenzoate (3)

6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl 2,5-diethynylbenzoate (**3**) was synthesized as follows. Into a 100 mL three-necked flask were added compound (**2**) (1.17 g, 1.79 mmol), $\text{PdCl}_2(\text{TPP})_2$ (25.1 mg, 0.04 mmol), CuI (3.4 mg, 0.02 mmol), 10 mL Et_3N and 15 mL THF under argon. After continuous stirring, trimethylsilylacetylene (0.53 g, 5.38 mmol) and 5 mL THF was added to the solution. After 30 min, the solution was heated to 65 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed

with water and extracted with CHCl_3 (3 \times). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, $\text{CHCl}_3/\text{hexane} = 1 : 2$ as eluent). The product (0.95, 1.61 mmol) was evaporated and dried and was added to a 100 mL round-bottom flask along with glacial acetic acid (0.19 g, 3.22 mmol), and 20 mL THF. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and TBAF (1.26 g, 4.84 mmol) was added dropwise to the solution in the flask. After continuous stirring for 1 hour, the solution was then evaporated and the residue was thoroughly washed with water and extracted with CHCl_3 (3 \times). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and recrystallized in EtOH. The product was evaporated and dried under vacuum to give compound (**3**) (0.66 g, 1.48 mmol) as a yellow powder. Yield = 83%.

Anal. Chemical Formula: $(\text{C}_{30}\text{H}_{25}\text{NO}_3)_n$ (447.53) $_n$: Calcd. C, 80.51; H, 5.63; O, 10.72; N, 3.13. Found C, 80.16, H, 5.60; N, 3.15. ^1H NMR (400 MHz, CDCl_3): δ = 1.50–1.62, 1.78–1.90 (m, 8H, $\text{HO}-\text{CH}_2(\text{CH}_2)_4\text{CH}_2-\text{Ar}$), 3.21 (s, 1H, $\text{H}\equiv\text{C}-\text{Ar}$ *ortho* to $-\text{COO}(\text{CH}_2)_6-\text{Ar}$), (s, 1H, $\text{H}\equiv\text{C}-\text{Ar}$ *meta* to $-\text{COO}(\text{CH}_2)_6-\text{Ar}$), 4.02 (t, 2H, $J = 6.4$ Hz, $\text{HO}-\text{CH}_2(\text{CH}_2)_4\text{CH}_2-\text{Ar}$), 4.37 (t, 2H, $J = 6.5$ Hz, $\text{HO}-\text{CH}_2(\text{CH}_2)_4\text{CH}_2-\text{Ar}$), 6.98 (d, 2H, $J = 8.8$ Hz, $\text{Ar}-\text{H}$ *ortho* and *para* to $-\text{COO}(\text{CH}_2)_6-\text{Ar}$), 7.51–7.57 (m, 4H, $\text{Ar}-\text{H}$ *ortho* and *meta* to $-\text{COO}-(\text{CH}_2)_6\text{O}-$), 7.63–7.70 (m, 4H, $\text{Ar}-\text{H}$ *ortho* and *meta* to $-\text{C}\equiv\text{N}$), 8.05 (m, 1H, $\text{Ar}-\text{H}$ *meta* to $-\text{COO}(\text{CH}_2)_6-\text{Ar}$). ^{13}C NMR (100 MHz, CDCl_3): δ = 22.2, 30.1, 31.4, 65.0, 72.1, 81.3, 83.1, 102.7, 113.0, 118.8, 124.4, 127.1, 129.8, 132.8, 146.8, 149.8.

LC-PPE

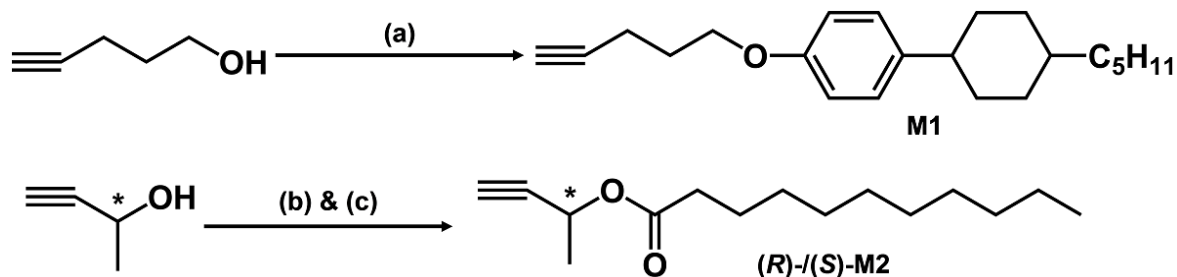
LC-PPE was synthesized as follows. Into a schlenk flask were added compound (**2**) (0.1 g, 0.15 mmol), CuI (1.17 mg, 6.14 μmol), $\text{PdCl}_2(\text{TPP})_2$ (2.16 mg, 3.1 μmol), and 2.5 mL THF under argon. After continuous stirring for 10 min, (**3**) (0.07 g, 0.15 mmol) and 1.0 mL THF was added to the reaction solution. Then 1.0 mL Et_3N was added dropwise into the reaction solution. After continuous stirring for 30 min, the solution was heated to 70 $^\circ\text{C}$ and left overnight. The mixture was cooled to room temperature, dissolved with CHCl_3 and was added dropwise to 500 mL of MeOH under stirring. The polymer precipitate was stirred for 24 h then filtered and dried in vacuo. A

yellow powder was obtained with a yield of 80% (0.05 g, 0.12 mmol). M_w . 15,400 M_w/M_n . 2.1 (GPC, PS calibration).

Anal. $(C_{29}H_{27}NO_3)_n$ (437.54) $_n$: Calcd. C, 79.61; H, 6.22; O, 10.97; N, 3.20. Found: C, 73.19; H, 5.52; N, 2.95. 1H NMR (400 MHz, $CDCl_3$): δ = 1.35–1.55, 1.65–1.92 (br, 8H, $HO-CH_2(CH_2)_4CH_2-Ar$), 3.83–4.11 (br, 2H, $HO-CH_2(CH_2)_4CH_2-Ar$), 4.18–4.57 (br, 2H, $HO-CH_2(CH_2)_4CH_2-Ar$), 6.80–7.10 (br, 2H, Ar-H *ortho* and *para* to $-COO(CH_2)_6-Ar$), 7.42–7.84 (br, 8H, Ar-H *ortho* and *meta* to $-COO-(CH_2)_6O-$, and Ar-H *ortho* and *meta* to $-C\equiv N$), 8.07–8.28 (m, 1H, Ar-H *meta* to $-COO(CH_2)_6-Ar$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.8, 26.0, 29.1, 35.6, 67.7, 89.7, 96.5, 114.5, 115.0, 115.4, 118.5, 127.0, 128.5, 132.6, 138.9, 146.5, 152.3, 162.1.

2. Supporting Information Schemes, Figures, and Tables

Scheme S1. Synthetic route of the monomers.^a

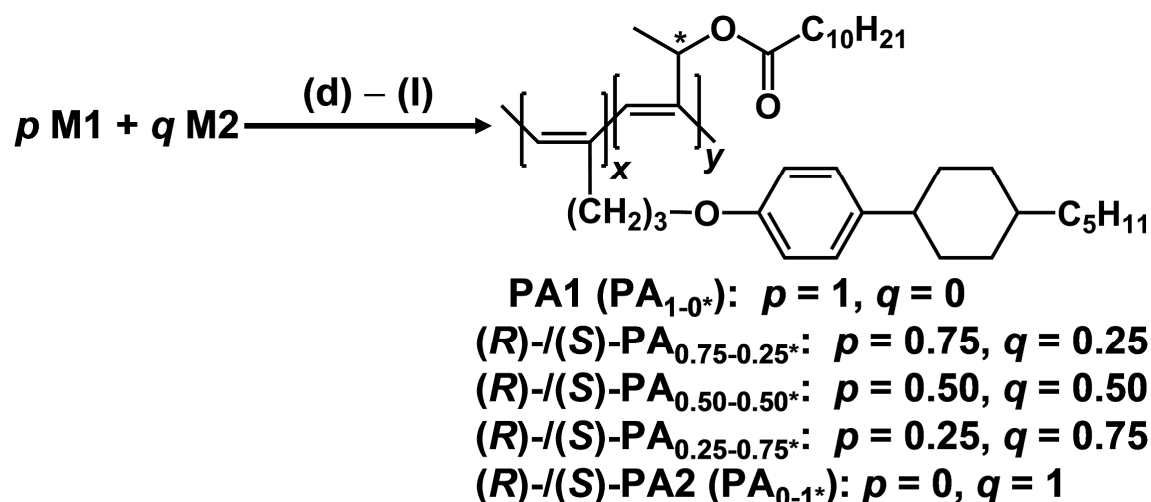


^aConditions: **Monomers:** (a) *para-trans*-4-*n*-pentyl(cyclohexyl) phenol, 4-pentyn-1-ol, TPP, DIAD, THF, r.t., 24 h; 66% for **M1**; (b) *n*-undecanoic acid, *(R)*-(+)-3-butyn-2-ol, DCC, DMAP, CH₂Cl₂, r.t., 24 h; 86% for **(R)-M2**; (c) *n*-undecanoic acid, *(S)*-(-)-3-butyn-2-ol, DCC, DMAP, CH₂Cl₂, r.t., 24 h; 97% for **(S)-M2**.

TPP = triphenylphosphine, DIAD = diisopropylazodicarboxylate,

DCC = *N,N'*-dicyclohexylcarboimide, DMAP = 4-dimethylaminopyridine

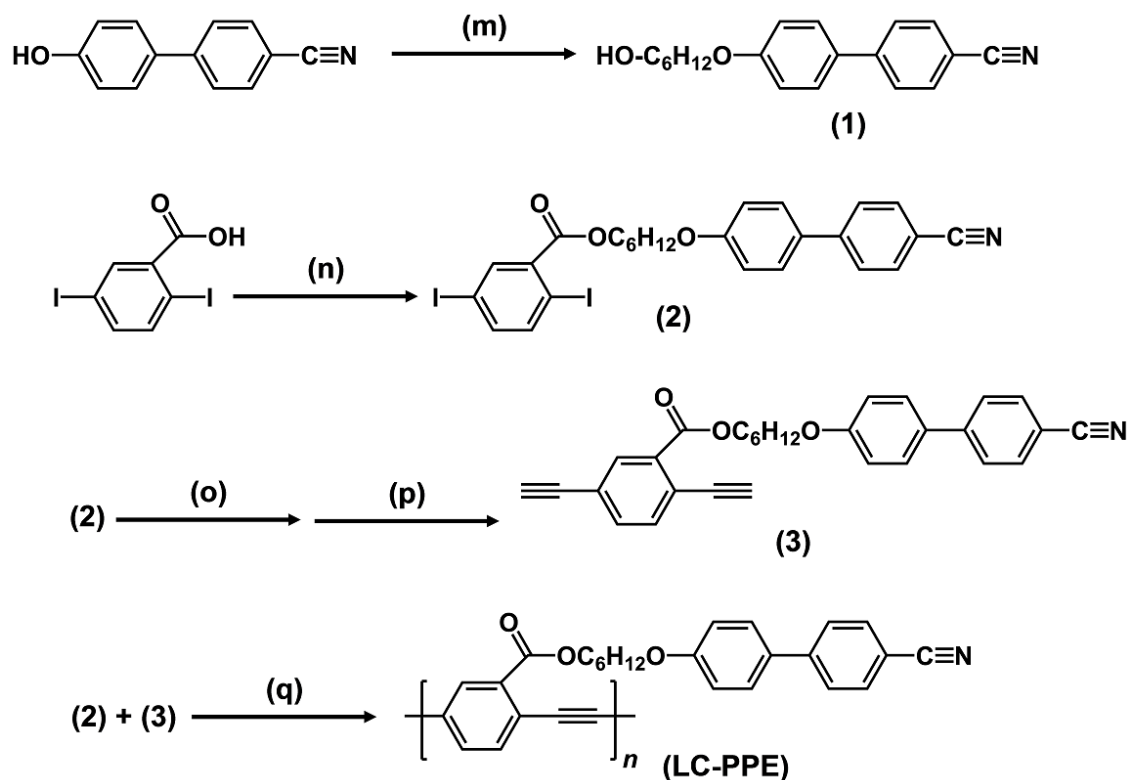
Scheme S2. Synthetic route of the *mono-PA* copolymers.



Polymers: (d) **M1**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 38% for **PA1**; (e) **M1**, (**R**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 49% for (**R**)-**PA0.75-0.25***; (f) **M1**, (**S**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 46% for (**S**)-**PA0.75-0.25***; (g) **M1**, (**R**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 71% for (**R**)-**PA0.50-0.50***; (h) **M1**, (**S**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 66% for (**S**)-**PA0.50-0.50***; (i) **M1**, (**R**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 77% for (**R**)-**PA0.25-0.75***; (j) **M1**, (**S**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 80% for (**S**)-**PA0.25-0.75***; (k) (**R**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 74% for (**R**)-**PA2**; (l) (**S**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 84% for (**S**)-**PA2**.

[Rh(nbd)Cl]₂ = Bicyclo[2.2.1] (hepta-2,5-diene)chlororhodium(I) dimer

Scheme S3. Synthetic route of the **LC-PPEs**.



Monomers: (m) 4'-hydroxy-4-cyano-biphenyl, 6-bromo-1-hexanol, acetone, THF, 60 °C, 24 h; 60% for **1**; (n) 2,5-diiodobenzoic acid, **1**, DCC, DMAP, CH₂Cl₂, r.t., 24 h; 73% for **2**; (o) **2**, PdCl₂(TPP)₂, CuI, Et₃N, trimethylsilylacetylene, THF, 65 °C, 24 h; (p) glacial acetic acid, THF, TBAF, 0 °C, 1 h; 83% for **3**; **Polymer:** (q) **2**, **3**, PdCl₂(TPP)₂, CuI, Et₃N, THF, 70 °C, 24 h; 80% for **LC-PPE**.

PdCl₂(TPP)₂ = *trans*-dichlorobis(triphenylphosphine)-palladium(II)

TBAF = tetra-*n*-butylammonium fluoride

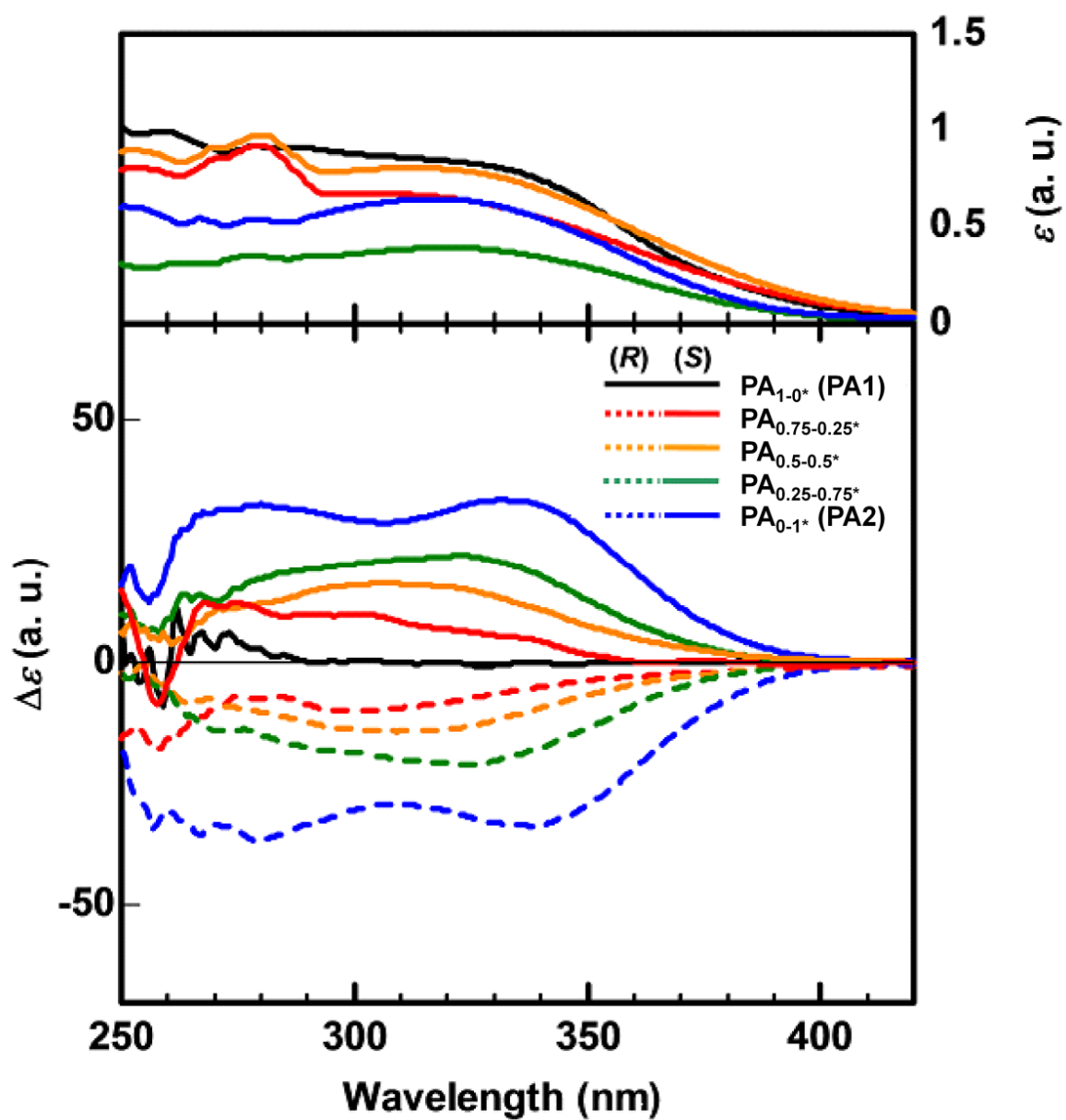


Figure S1. UV-vis (above) and CD spectra (below) of the *mono*-substituted polyacetylene copolymers in annealed cast film.

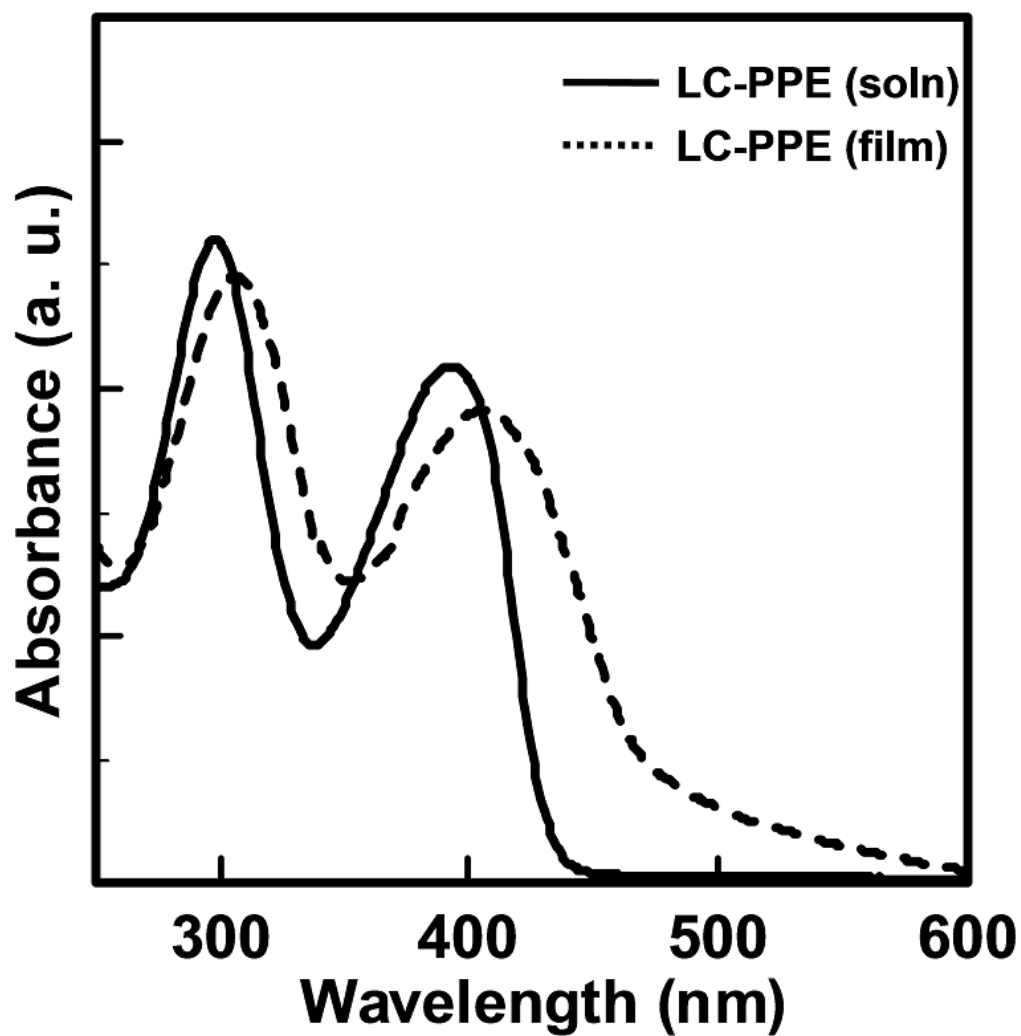


Figure S2. UV-vis of the LC-substituted poly(*para*-phenylene ethynylene) in solution (solid line) and in cast film (dashed line).