

Electronic Supplementary Information

Oligo(Ethylene Glycol)-incorporating Hybrid Linear Alkyl Side Chains for n-channel Polymer Semiconductors and Its Effect on Thin-Film Crystalline Structure.

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Experimental Section

Materials

All starting materials were purchased from Aldrich, TCI and Alfa Aesar. Pd catalyst was purchased from Umicore. All starting materials were used without further purification. 4,9-Dibromoisochromeno[6,5,4-*def*]isochromene-1,3,6,8-tetraone and (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene were synthesized according to a method reported previously in the literature.^{S1}

Synthesis

1. Synthesis of tetraethylene glycol ditosylate (1)

Tetraethylene glycol (8.89 mL, 51.49 mmol) was dissolved in anhydrous chloroform (60 mL). The solution was cooled to $-20\text{ }^{\circ}\text{C}$ in a sodium chloride ice bath. Tosyl chloride (29.45 g, 154.47 mmol) and anhydrous pyridine (53.72 mL) were added sequentially while keeping the temperature of the solution below $0\text{ }^{\circ}\text{C}$. After 5 h reaction at $-20\text{ }^{\circ}\text{C}$, chloroform and pyridine were removed under reduced pressure. Ice water was added and the solution was extracted with CH_2Cl_2 three times. The combined organic phase was washed twice with 2N HCl, 5% NaHCO_3 solution and water sequentially. After the organic layer was dried over MgSO_4 , the solvent was removed under reduced pressure. The residue was subjected to silica chromatography using EtOAc/hexane (1/2) to give product as colorless oil. Yield: 80% (20.70 g). ^1H NMR (300 MHz, CDCl_3 , δ): 7.82-7.80 (d, 4H), 7.37-7.34 (d, 4H), 4.19-4.15 (t, 4H), 3.71-3.68 (t, 4H), 3.58 (s, 8H), 2.46 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 144.84, 132.96, 129.84, 127.99, 70.74, 70.55, 69.26, 68.70, 21.66.

2. Synthesis of 3,6,9,12-tetraoxaicosyl 4-methylbenzenesulfonate (2)

Sodium hydride (60 % in mineral oil) (1.98 g, 82.38 mmol) was weighed under nitrogen and transferred into a 250 mL flask. Anhydrous DMF (10 mL) was added and the mixture was cooled in an ice bath. Octanol (5.36 g, 41.19 mmol) was added dropwise while keeping the solution below 0 °C. The reaction solution was stirred at room temperature for 1 h until all of the solids dissolved and the solution turned yellow. Tetraethylene glycol ditosylate (20.70 g, 82.38 mmol) was dissolved in DMF (50 mL) and added to the reaction mixture at -20 °C with vigorous stirring. The solution was warmed to room temperature and stirred overnight before it was quenched with water. The solvent was removed under vacuum and the residue was dissolved in water. The pH of the solution was adjusted to 7.0 with HCl, and then the aqueous solution was extracted with CH₂Cl₂ three times. The combined organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was subjected to silica chromatography using EtOAc/hexane (1/2) to give product as colorless oil. Yield: 40% (7.58 g). ¹H NMR (300 MHz, CDCl₃, δ): 7.82-7.80 (d, 2H), 7.37-7.34 (d, 2H), 3.71-3.56 (m, 16H), 3.47-3.43 (t, 2H), 2.46 (s, 3H), 1.64-1.56 (t, 2H), 1.28 (m, 10H), 0.89-0.86 (t, 3H); ¹³C NMR (75 MHz, CDCl₃, δ): 144.84, 139.32, 130.96, 129.84, 70.74, 70.55, 69.96, 66.89, 32.01, 30.35, 29.96, 29.37, 29.20, 23.05, 21.27, 14.17.

3. Synthesis of 2-(3,6,9,12-tetraoxaicosyl)isoindoline-1,3-dione (3)

3,6,9,12-Tetraoxaicosyl-4-methylbenzenesulfonate (8.58 g, 18.63 mmol) and potassium phthalimide (3.80 g, 20.49 mmol) were dissolved in DMF (20 mL). The reaction solution was stirred at 80 °C overnight. After cooling to room temperature, the reaction mixture was diluted with CH₂Cl₂ and filtered. The white precipitate was washed further twice with CH₂Cl₂. The combined organic solution was washed with NaOH aqueous solution (0.1 M) and brine sequentially. After removal of solvent under reduced pressure, the residue was subjected to silica chromatography using EtOAc/hexane (1/2) to give the product as yellow

oil. Yield: 80% (6.49 g). ¹H NMR (300 MHz, CDCl₃, δ): 7.87-7.81 (m, 2H), 7.74-7.68 (m, 2H), 3.89-3.88 (m, 2H), 3.75-3.73 (m, 2H), 3.66-3.57 (m, 12H), 3.45-3.41 (m, 2H), 1.58-1.51 (t, 2H), 1.26-1.18 (m, 10H), 0.89-0.84 (m, 3H); ¹³C NMR (75 MHz, CDCl₃, δ): 166.89, 133.16, 132.01, 124.78, 70.77, 70.39, 69.94, 66.69, 41.01, 31.92, 29.86, 29.26, 22.76, 14.06.

4. Synthesis of 3,6,9,12-tetraoxaicosan-1-amine (4)

2-(3,6,9,12-Tetraoxaicosyl)isoindoline-1,3-dione (6.49 g, 14.90 mmol), hydrazine hydrate (1.43 mL, 46.19 mmol) and 60 mL methanol were stirred at 95 °C and monitored by TLC. After disappearance of the starting imide, the methanol was evaporated under reduced pressure, the residue diluted with CH₂Cl₂ and washed with 10% KOH. Aqueous layers were combined and extracted with CH₂Cl₂. The combined organic layers were washed with brine and dried over MgSO₄. The removal of CH₂Cl₂ afforded pure yellow oil as product which was used without further purification. Yield: 76% (3.46 g). ¹H NMR (300 MHz, CDCl₃, δ): 3.68-3.65 (m, 16H), 3.47 (t, 2H), 2.91 (br s, 2H), 1.62-1.57 (m, 2H), 1.27-1.21 (m, 10H), 0.92-0.85 (t, 3H); ¹³C NMR (75 MHz, CDCl₃, δ): 71.50, 70.52, 70.00, 69.77, 66.58, 37.69, 37.06, 31.79, 30.01, 29.68, 29.41, 29.23, 26.05, 22.62, 14.07.

5. Synthesis of octane-1,8-diyl bis(4-methylbenzenesulfonate) (5)

Octane-1,8-diol (10.00 g, 68.39 mmol) was dissolved in 50 mL of pyridine. The solution was cooled to 0°C and then tosyl chloride (33.77 g, 177.13 mmol) was added over a period of 30 min. The mixture was stirred for 3 h at 0 °C and then poured into ice water. The white solid precipitate was filtered and dried. Yield: 63% (19.64 g). ¹H NMR (300 MHz, CDCl₃, δ): 7.82-7.79 (d, 4H), 7.38-7.35 (d, 4H), 4.04-4.00 (t, 4H), 2.47 (s, 6H), 1.67-1.58 (m, 4H), 1.31-1.20 (m, 8H); ¹³C NMR (75 MHz, CDCl₃, δ): 144.69, 133.17, 129.83, 127.88, 70.55, 28.74, 28.67, 25.19, 21.65.

6. Synthesis of 2,5,8,11-tetraoxanonadecan-19-yl 4-methylbenzenesulfonate (6)

Sodium hydride (60 % in mineral oil, 1.80 g, 75.18 mmol) was weighed under nitrogen and transferred into a 250 mL flask. Anhydrous DMF (10 mL) was added and the mixture was cooled in an ice bath. Triethylene glycol monomethyl ether (6.01 mL, 37.59 mmol) was added dropwise while keeping the solution below 0 °C. The reaction solution was stirred at room temperature for 1 h until all of the solids dissolved and the solution turned yellow. Octane-1,8-diyl bis(4-methylbenzenesulfonate) (17.09 g, 37.59 mmol) was dissolved in DMF (50 mL) and added to the reaction mixture at -20 °C with vigorous stirring. The solution was warm to room temperature and stirred overnight before it was quenched with water. The solvent was removed under vacuum and the residue was dissolved in water. The pH of the solution was adjusted to 7.0 with HCl, and then the aqueous solution was extracted with CH₂Cl₂ three times. The combined organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was subjected to silica chromatography using EtOAc/hexane (1/2) to give product as colorless oil. Yield: 41% (6.88 g). ¹H NMR (300 MHz, CDCl₃, δ): 7.82-7.80 (d, 2H), 7.34-7.31 (d, 2H), 3.69-3.62 (m, 10H), 3.58-3.53 (m, 4H), 3.49-3.44 (t, 2H), 3.42 (s, 3H), 2.57 (s, 3H), 1.71-1.70 (m, 2H), 1.69-1.64 (m, 2H), 1.32-1.30 (m, 8H); ¹³C NMR (75 MHz, CDCl₃, δ): 144.57, 139.63, 132.05, 127.97, 71.65, 70.71, 70.44, 70.13, 69.85, 59.37, 30.24, 29.63, 28.63, 25.21, 21.47.

7. Synthesis of 2-(2,5,8,11-tetraoxanonadecan-19-yl)isoindoline-1,3-dione (7)

2,5,8,11-Tetraoxanonadecan-19-yl 4-methylbenzenesulfonate (6.00 g, 13.43 mmol) and potassium phthalimide (2.74 g, 14.78 mmol) were dissolved in DMF (30 mL). The reaction solution was stirred at 80 °C overnight. After cooling to room temperature, the reaction

mixture was diluted with CH₂Cl₂ and filtered. The white precipitate was washed further twice with CH₂Cl₂. The combined organic solution was washed with NaOH aqueous solution and brine sequentially. After removal of solvent under reduced pressure, the residue was subjected to silica chromatography using EtOAc/hexane (1/2) to give the product as yellow oil. Yield: 75% (4.25 g). ¹H NMR (300 MHz, CDCl₃, δ): 7.87-7.85 (m, 2H), 7.74-7.71 (m, 2H), 3.71-3.64 (m, 10H), 3.60-3.55 (m, 4H), 3.47-3.43 (t, 2H), 3.40 (s, 3H), 1.70-1.67 (m, 2H), 1.62-1.58 (m, 2H), 1.33-1.32 (m, 8H); ¹³C NMR (75 MHz, CDCl₃, δ): 167.91, 132.21, 132.03, 123.68, 72.06, 70.74, 70.42, 70.11, 58.98, 40.61, 31.94, 30.02, 29.64, 29.22, 29.14, 26.57.

8. Synthesis of 2,5,8,11-tetraoxanonadecan-19-amine (8)

2-(2,5,8,11-Tetraoxanonadecan-19-yl)isoindoline-1,3-dione (4.13 g, 8.51 mmol), hydrazine hydrate (0.82 mL, 26.38 mmol) and 20 mL methanol were stirred at 95 °C and monitored by TLC. After disappearance of the starting imide, the methanol was evaporated under reduced pressure, the residue diluted with CH₂Cl₂ and washed with 10% KOH. Aqueous layers were combined and extracted with CH₂Cl₂. The combined organic layers were washed with brine and dried over MgSO₄. The removal of CH₂Cl₂ afforded pure yellow oil as product which was used without further purification. Yield: 77% (1.91 g). ¹H NMR (300 MHz, CDCl₃, δ): 3.68-3.65 (m, 10H), 3.61-3.57 (m, 4H), 3.46 (t, 2H), 3.40 (s, 3H), 2.05 (br s, 2H), 1.61-1.57 (m, 2H), 1.54-1.49 (m, 2H), 1.32 (m, 8H); ¹³C NMR (75 MHz, CDCl₃, δ): 71.63, 70.65, 70.41, 70.12, 59.32, 42.03, 32.68, 30.28, 30.07, 29.65, 29.36, 29.25, 26.71.

9. Synthesis of 4,9-dibromo-2,7-di(3,6,9,12-tetraoxaicosyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (9)

4,9-Dibromoisochromeno[6,5,4-*def*]isochromene-1,3,6,8-tetraone (NDA-Br₂) (2.00 g, 4.67 mmol) and 3,6,9,12-tetraoxaicosan-1-amine (3.14 g, 10.27 mmol) were added in acetic acid (20 mL). The reaction mixture was refluxed under N₂ for 1 h. Then the reaction mixture was poured onto water and the resulting precipitate is filtered and washed with methanol. The crude product was purified via column chromatography over silica gel (eluent: dichloromethane/hexane = 1/1). Monomer (**9**) was obtained as an orange solid. Yield: 25 % (1.17 g). ¹H NMR (300MHz, CDCl₃, δ): 8.88 (s, 2H), 3.88-3.87 (m, 4H), 3.74-3.73 (m, 4H), 3.67-3.59 (m, 24H), 3.47-3.42 (m, 4H), 1.59-1.53 (t, 4H), 1.27-1.20 (m, 20H), 0.88-0.85 (m, 6H); ¹³C NMR (75 MHz, CDCl₃, δ): 160.32, 143.96, 136.66, 135.57, 130.62, 119.31, 70.68, 70.44, 70.13, 65.34, 41.01, 30.99, 29.98, 29.62, 29.27, 22.75, 14.07; HR-MS: calcd. 998.3139, found. 998.3720.

10. Synthesis of 4,9-dibromo-2,7-di(2,5,8,11-tetraoxanonadecan-19-yl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (10)

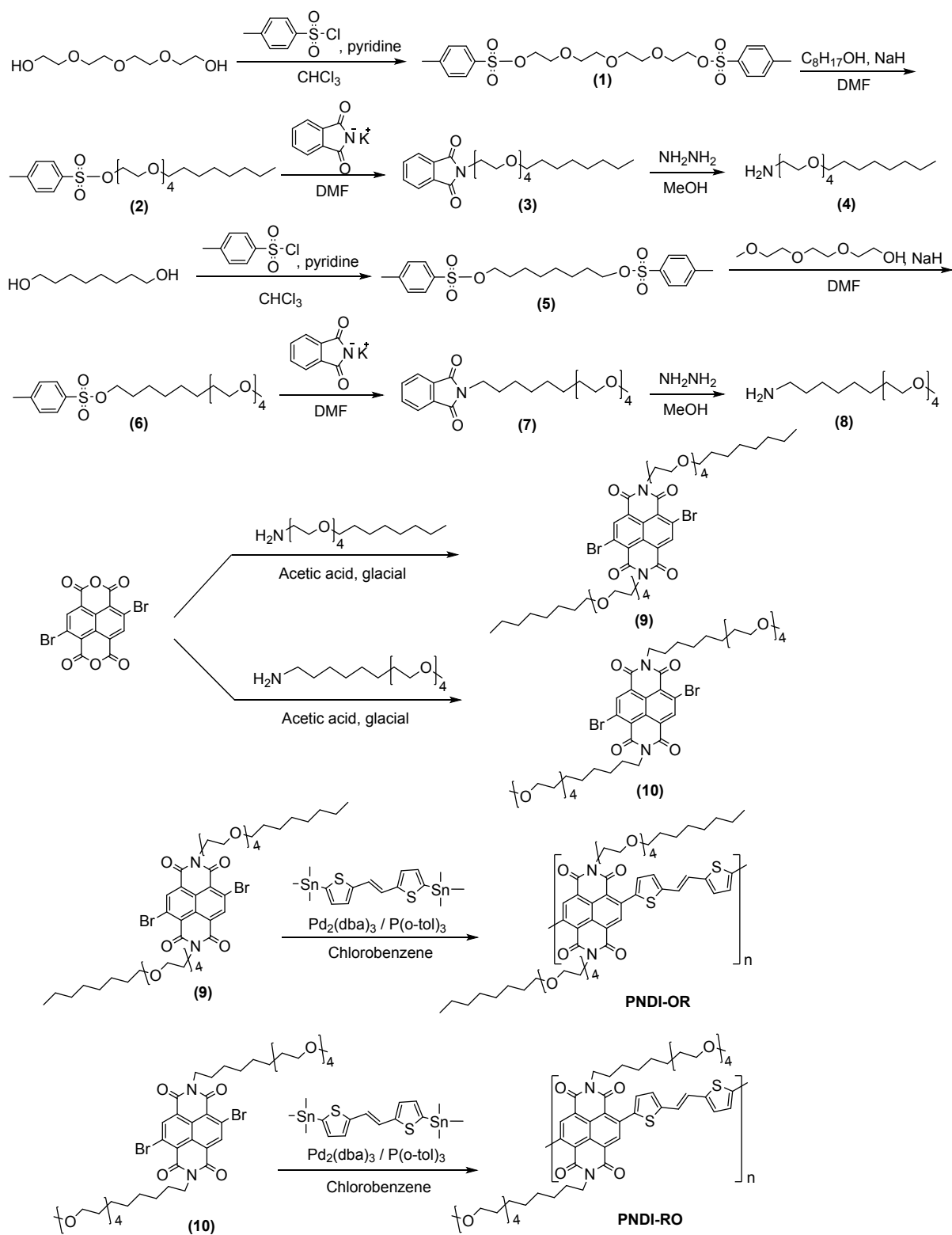
4,9-Dibromoisochromeno[6,5,4-*def*]isochromene-1,3,6,8-tetraone (NDA-Br₂) (1.29 g, 3.02 mmol) and 2,5,8,11-tetraoxanonadecan-19-amine (1.94 g, 6.64 mmol) were added 15 mL of glacial acid. The reaction mixture was refluxed under N₂ for 1 h. Then the reaction mixture was poured onto water and the resulting precipitate is filtered and washed with methanol. The crude product was purified via column chromatography over silica gel (eluent: dichloromethane/hexane = 1/1). Monomer (**10**) was obtained as an orange solid. Yield: 27% (0.79 g). ¹H NMR (300MHz, CDCl₃, δ): 8.99 (s, 2H), 3.68-3.65 (m, 20H), 3.61-3.56 (m, 8H), 3.48-3.43 (t, 4H), 3.39 (m, 6H), 1.73-1.72 (m, 4H), 1.58-1.56 (m, 4H), 1.33-1.17 (m, 16H); ¹³C NMR (75 MHz, CDCl₃, δ): 160.65, 145.05, 136.66, 135.41, 130.49, 120.34, 72.01, 70.65, 70.39, 69.98, 58.99, 39.47, 30.26, 29.97, 29.67, 29.33, 29.25, 27.05; HRMS: calcd. 970.2826, found. 970.2922.

11. Synthesis of poly[(*E*)-2,7-di(3,6,9,12-tetraoxaicosyl)-4-methyl-9-(5-(2-(5-methylthiophen-2-yl)vinyl)thiophen-2-yl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone] (PNDI-OR)

The polymer was prepared from a palladium catalyzed Stille coupling reaction. 4,9-Dibromo-2,7-di(3,6,9,12-tetraoxaicosyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (0.50 g, 0.50 mmol) and (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (0.26 g, 0.50 mmol) were dissolved in dry chlorobenzene (7.5 mL). After degassed with nitrogen for 1 h, Pd₂(dba)₃ (9.20 mg) and P(*o*-Tol)₃ (12.20 mg) added to the mixture and stirred for 48 h at 110 °C. 2-Bromothiophene and tributyl(thiophen-2-yl)stannane were added successively at a time interval of 6 h to end-cap the endgroups, respectively. The polymer was precipitated in methanol. The crude polymer was collected by filtration and then purified by Soxhlet extraction with methanol, acetone, hexane, toluene and chloroform, successively. The final product was obtained by precipitation in methanol and drying in vacuo. PNDI-OR was obtained as a dark green solid. Yield: 79% (0.42 g). M_n = 16,511, M_w = 45,301, PDI = 2.74). ¹H NMR (500 MHz, CDCl₃, δ): 8.52 (br, 2H), 7.50-7.18 (br, 6H), 3.89 (m, 4H), 3.75-3.71 (m, 4H), 3.66-3.61 (m, 24H), 3.45-3.42 (m, 4H), 1.60-1.55 (br, 4H), 1.28-1.20 (m, 20H), 0.90-0.83 (m, 6H). IR (KBr, cm⁻¹): ν = 2952, 2922, 2851, 1704, 1666, 1197.

12. Synthesis of Poly[(*E*)-4-methyl-9-(5-(2-(5-methylthiophen-2-yl)vinyl)thiophen-2-yl)-2,7-di(2,5,8,11-tetraoxanonadecan-19-yl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone] (PNDI-RO)

The polymer was prepared from a palladium catalyzed Stille coupling reaction. 4,9-Dibromo-2,7-di(2,5,8,11-tetraoxanonadecan-19-yl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (0.50 g, 0.51 mmol) and (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (0.27 g, 0.51 mmol) were dissolved in dry chlorobenzene (7.5 mL). After degassed with nitrogen for 1 h, Pd₂(dba)₃ (9.40 mg) and P(*o*-Tol)₃ (12.50 mg) added to the mixture and stirred for 48 h at 110 °C. 2-Bromothiophene and tributyl(thiophen-2-yl)stannane were added successively at a time interval of 6 h to end-cap the endgroups, respectively. The polymer was precipitated in methanol. The crude polymer was collected by filtration and then purified by Soxhlet extraction with methanol, acetone, hexane, toluene and chloroform, successively. The final product was obtained by precipitation in methanol and drying in vacuo. PNDI-RO was obtained as a dark green solid. Yield: 75% (0.42 g). M_n = 24,281, M_w = 70,209, PDI = 2.89). ¹H NMR (500 MHz, CDCl₃, δ): 8.83-8.49 (br, 2H), 7.34-7.19 (br, 6H), 3.69-3.66 (m, 20H), 3.60-3.56 (m, 8H), 3.47-3.45 (m, 4H), 3.38-3.37 (m, 6H), 1.72-1.71 (br, 4H), 1.58-1.55 (m, 4H), 1.32-1.15 (m, 16H). IR (KBr, cm⁻¹): ν = 2924, 2855, 1727, 1705, 1659, 1110.



Scheme S1. Synthetic routes of PNDI-OR and PNDI-RO.

Characterization

^1H NMR spectra were recorded using a Bruker Avance 300 MHz and Bruker DRX 500 FT-NMR spectrometer; chemical shifts (ppm) were reported with tetramethylsilane as an internal standard. Fourier transform (FT)-IR spectra were recorded using a Varian 640-IR spectrometer. Thermogravimetric analysis (TGA) was performed under N_2 using a TA instrument TGA Q50. Differential scanning calorimeter (DSC) was conducted under N_2 using a TA instrument DSC Q20, and both samples were heated at a rate of $10\text{ }^\circ\text{C min}^{-1}$. UV-vis spectra were measured using a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Mass spectrometry data were obtained with High Resolution GC Mass Spectrometer JMS-700 (Jeol). Cyclic voltammetry (CV) measurement was performed on CH instruments CHI 1000 with a three-electrode cell in a nitrogen bubbled 0.1 M tetrabutylammonium perchlorate (TBAP) solution in chloroform at room. Number-average (M_n) and weight average (M_w) molecular weights, and polydispersity index (PDI) of the polymers were determined by Advanced Polymer Chromatograph with ACQUITY APC System using a series of disperse polystyrene as standards in chloroform (HPLC grade).

The film morphologies were characterized with atomic force microscopy (AFM, VEECO Instruments Inc.). The thickness of polymer films was measured using an ellipsometer (M-2000V, J. A. Woollam Co., Inc.). 2D grazing incidence X-ray diffraction grazing incidence X-ray diffraction (GIXD) experiments were performed using the synchrotron source at the Pohang Accelerator Laboratory (PAL) in Korea. 2D GIXD patterns were recorded with a 2D CCD detector (Rayonix SX165) and X-ray irradiation time was 1 ~ 10 seconds dependent on the saturation level of detector. Diffraction angles were calibrated by a pre-calibrated sucrose (Monoclinic, P21, $a = 10.8631\text{ \AA}$, $b = 8.7044\text{ \AA}$, $c = 7.7624\text{ \AA}$, $\beta = 102.938^\circ$).^{S2}

Computational details

Density functional theory (DFT) calculations were performed using the Gaussian 09 package with the nonlocal hybrid Becke three-parameter Lee-Yang-Parr (B3LYP) function and the 6-31G* basis set after optimizing the geometry of oligomers.

PFET fabrication and measurements

PFET devices were prepared on an octadecyltrimethoxysilane (OTS)-treated surface prepared from a highly doped p-Si wafer with a 300 nm thick thermally grown oxide layer. The wafer served as a gate electrode, whereas the oxide layer acted as the gate dielectric (capacitance = 10.8 nF cm⁻²). The SiO₂/Si wafers were cleaned with piranha solution (a mixture of 70 vol% H₂SO₄ and 30 vol% H₂O₂), followed by UV-ozone treatment. The surface of the wafers was modified with OTS self-assembled monolayers.^{S3} The OTS solution (3 mM in trichloroethylene) was spin-coated at 3000 rpm for 30 s onto the wafers, and then the samples were kept overnight in a vacuum desiccator with a few drops of NH₄OH. The wafers were washed with toluene, acetone and isopropyl alcohol, and dried under nitrogen gas. The contact angle of deionized water on the OTS-treated SiO₂ was typically above 110°. Then the semiconducting polymer films were spin-coated at 2000 rpm from a 0.5 wt% chloroform solution (~40 nm in thickness). The films were dried under a vacuum for 2 h. The source and drain electrodes (Au 70 nm) were thermally evaporated through shadow mask to define channel length and width, 150 μm and 1500 μm, respectively.

The electrical properties of the polymer field-effect transistor (PFET) devices were characterized at room temperature in a dark environment under a N₂ atmosphere using a Keithley 4200-SCS semiconductor parametric analyzer. The field-effect mobility (μ) and the threshold voltage (V_T) were estimated in the saturation regime ($V_D = 60$ V) with the following

equation:^{S4} $I_D = \frac{W}{2L} \mu C_g (V_G - V_T)^2$, where I_D is the drain current, C_g is the capacitance of the gate dielectric and V_G is the gate-source voltage.

All-polymer bulk-heterojunction solar cell fabrication and measurements

For the fabrication of all-polymer solar cell devices, indium tin oxide (ITO)-coated glass was used as the substrate. First, the ITO-coated glass was successively cleaned using detergent, water, acetone, and 2-propanol with ultrasonication. The cleaned surface was then subjected to UV-ozone treatment for 20 min. Next, a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron P VP AI 4083, Clevios) solution was spin-cast on the top of ITO-coated glass with a thickness of 30–40 nm. Then, PEDOT:PSS-coated ITO glass was baked in an oven at 120 °C for 30 min and transferred to a glove box. The acceptor polymer, PNDI-OR or PNDI-RO, was blended with a donor polymer, PTB7 (1-Materials Inc.) (1:1 w/w), in chlorobenzene (chloroform, o-xylene, or 1,2-dichlorobenzene) at a total concentration of 20 mg mL⁻¹. The photoactive blends were spin-cast on the prepared PEDOT:PSS-coated ITO glass and dried for 1 h under nitrogen. LiF (0.6 nm) and Al (120 nm) were thermally deposited as the cathode through a shadow mask. The current density–voltage characteristics were measured under AM1.5 solar illumination (Oriel 1 kW solar simulator) using a Keithley 4200 unit in a nitrogen-filled glove box.

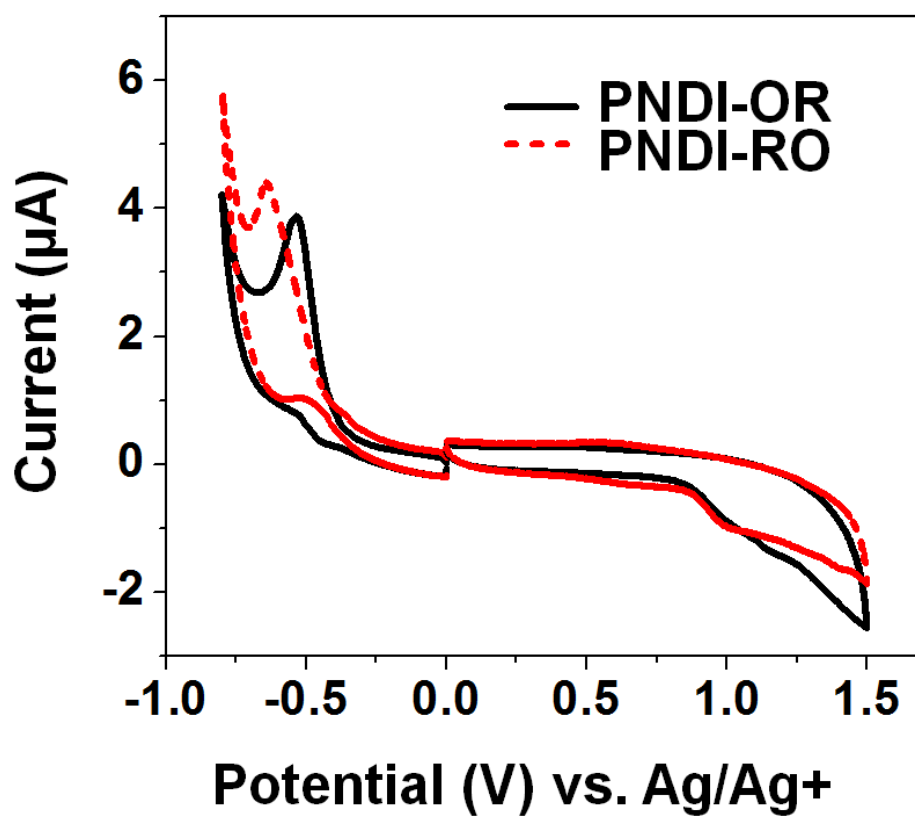


Figure S1. Cyclic voltammograms of PNDI-OR and PNDI-RO polymers.

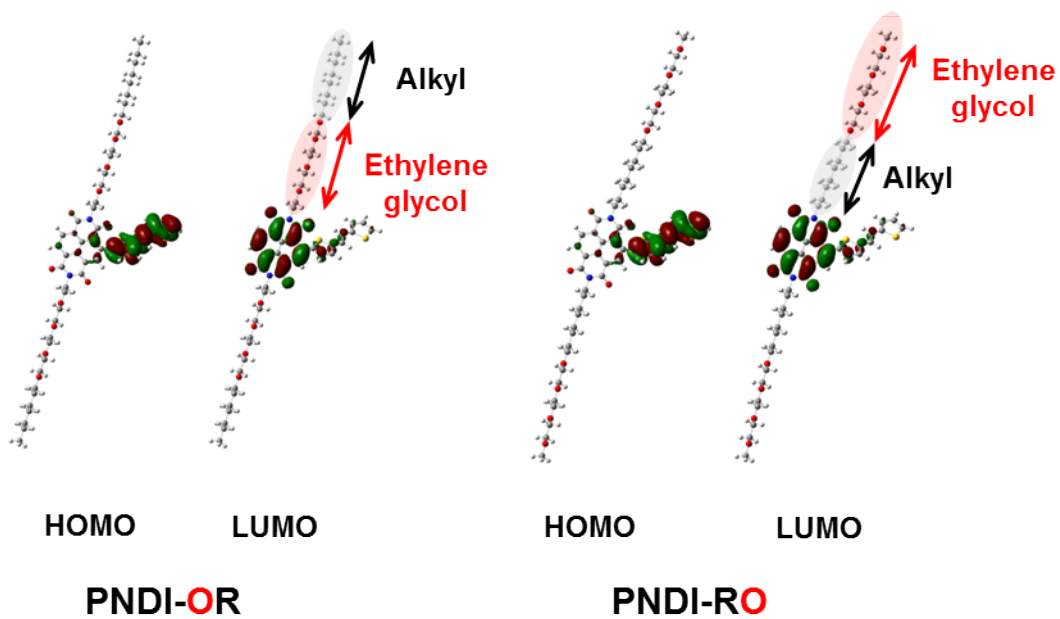


Figure S2. Calculated molecular orbitals for the model monomers of PNDI-OR and PNDI-RO.

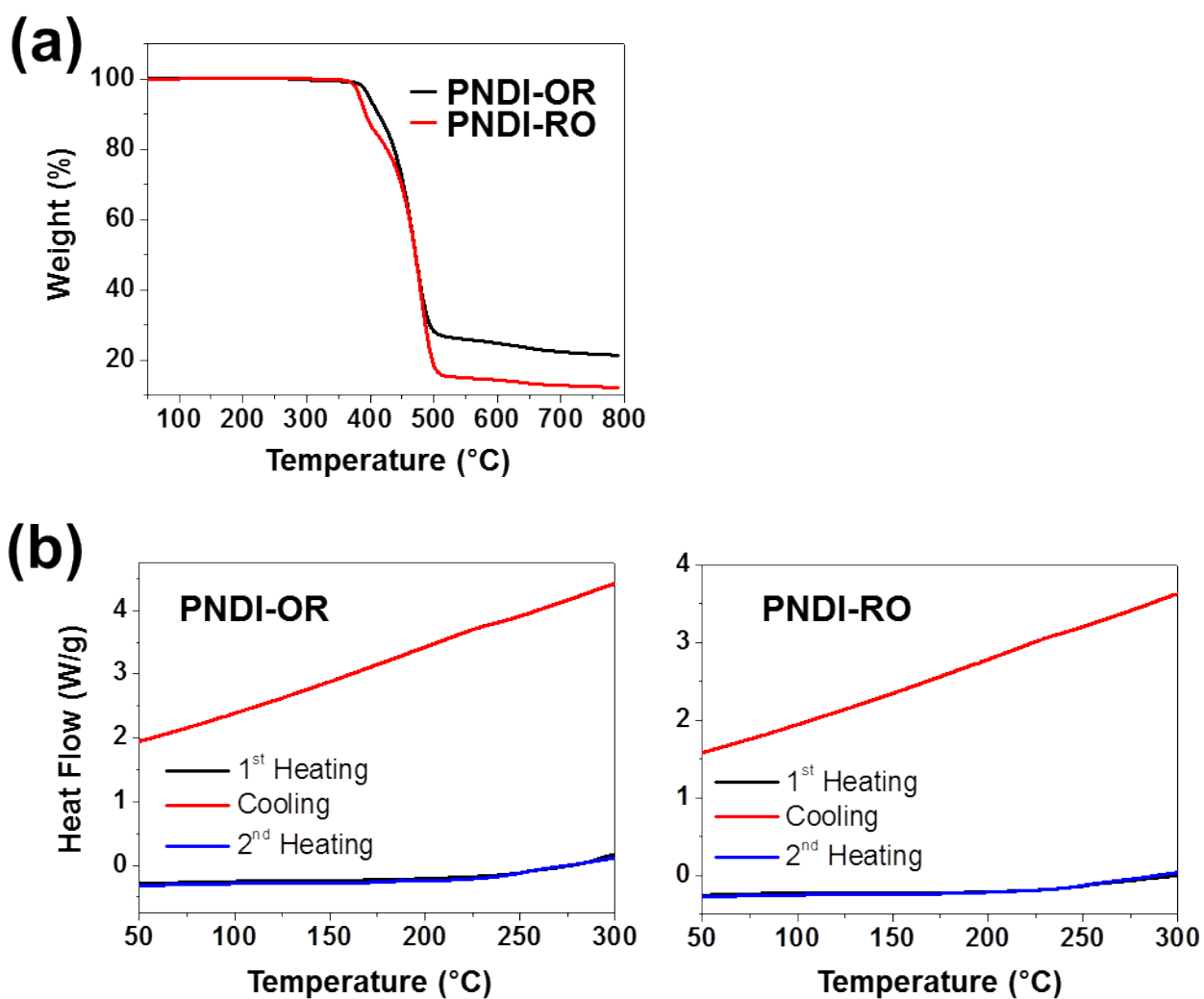


Figure S3. (a) Thermogravimetric analysis (TGA) plots and (b) differential scanning calorimetry (DSC) thermogram of polymers in a N₂ atmosphere at a scan rate of 10 °C min⁻¹.

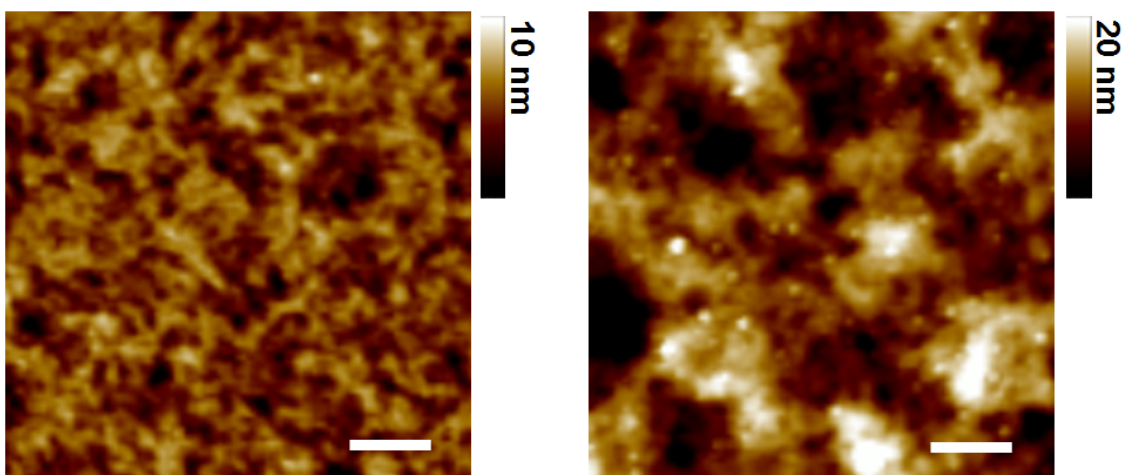


Figure S4. AFM height images of PNDI-OR (left) and PNDI-RO (right) films prepared using a 1-chloronaphthalene solvent additive, in which the scale bar is 200 nm.

Bias-stress stability test of PFETs

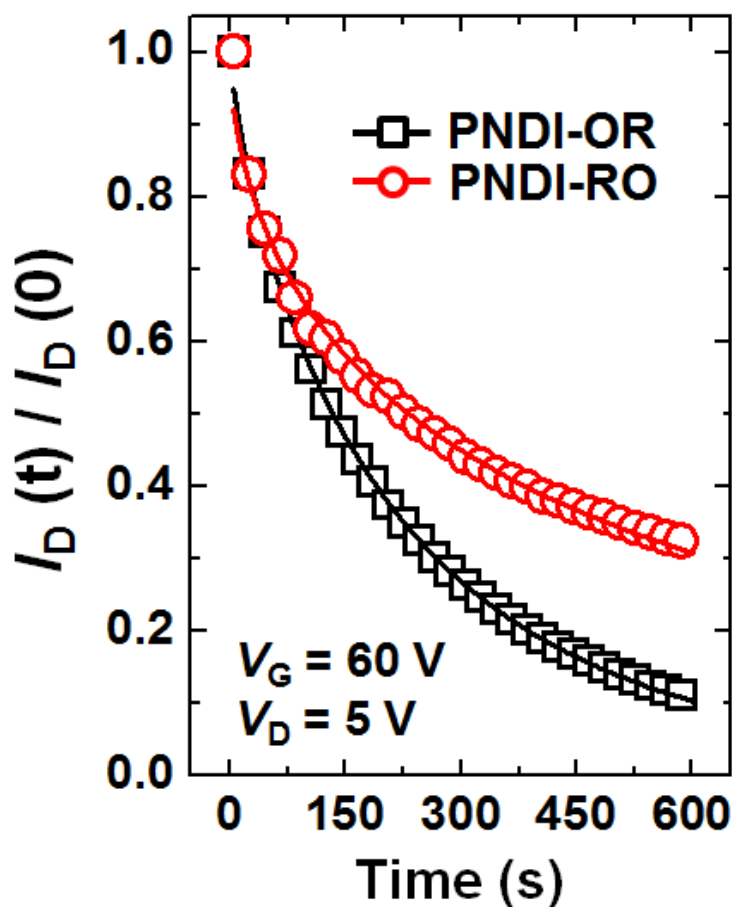


Figure S5. Normalized time-dependent drain-current (I_D) decay of the optimized PFETs under constant bias-stress ($V_G = 60 \text{ V}$, $V_D = 5 \text{ V}$) in vacuum. Experimental results (open symbol) are normalized with an initial drain-current value ($I_D(0)$) and are fitted with the stretched exponential function (solid line).

We examined the bias-stress stability of the annealed PFET devices. The time-dependent I_D decay was measured under a constant bias stress of $V_G = 60 \text{ V}$ and $V_D = 5 \text{ V}$ in vacuum. The continuous decay of I_D results from bias-induced charge trapping. Interestingly, the PNDI-RO FETs exhibited more stable operation than did the PNDI-OR FETs. Quantitative analysis was conducted by the stretched-exponential formula, which is a

representative model for analyzing the bias-stress effect:^{S5} $I_D(t) = I_D(0) \exp[-(t/\tau)^\beta]$, where τ is a characteristic time and β is a dispersion parameter. The extracted parameters were substantially different between the PNDI-RO and PNDI-OR FETs: $\tau = 447$ s/ $\beta = 0.79$ for PNDI-RO, and $\tau = 212$ s/ $\beta = 0.56$ for PNDI-OR. The larger τ and β values of the PNDI-RO FETs compared to those of the PNDI-OR FETs indicate that a lower density of charge traps and/or higher barriers for charge trapping are induced under bias stress in the PNDI-RO FETs.^{S5} Further, it implies that the energy barrier for charge trapping has a relatively narrow distribution in PNDI-RO. The better bias-stress stability of PNDI-RO FETs is presumably attributed to the aforementioned superior crystalline ordering and the difference in the chemical structure of the side chains. The origin of the different bias stress stabilities of the polymers is a topic for further investigation.

Results of All-polymer bulk-heterojunction solar cells

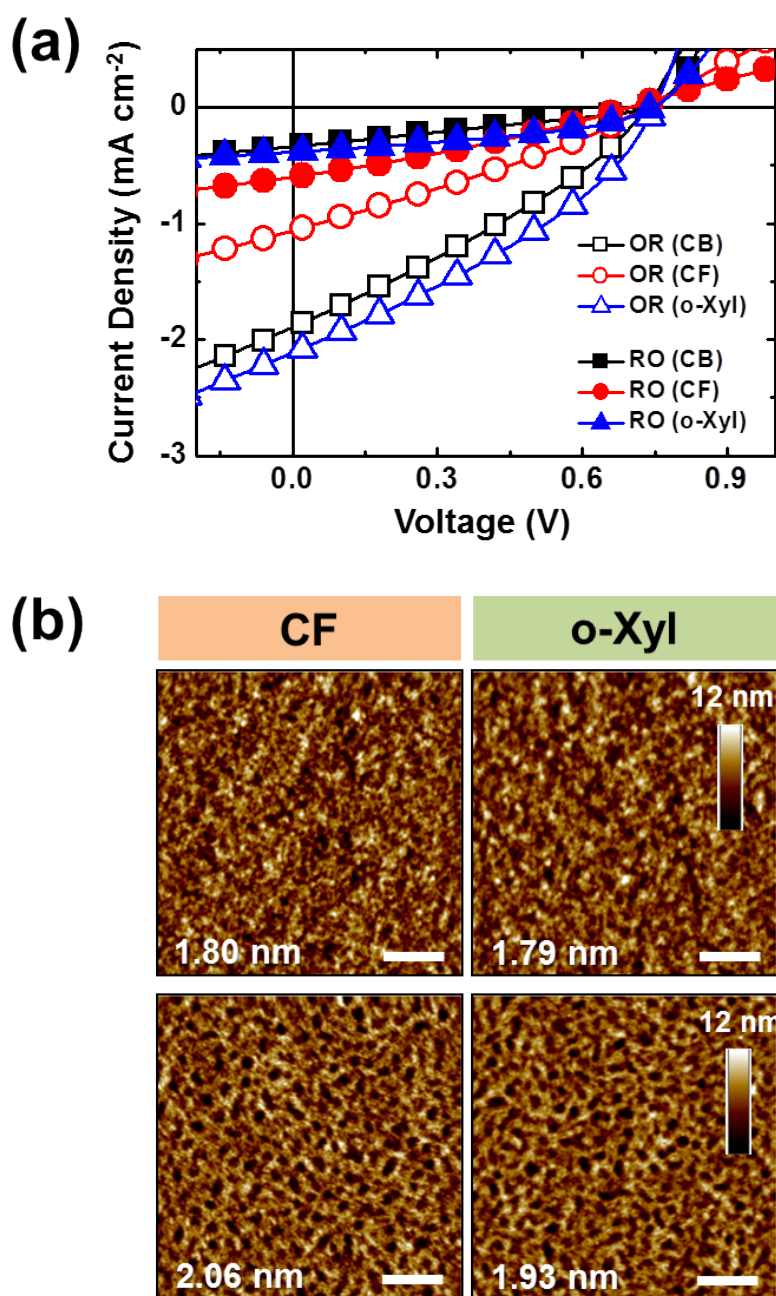


Figure S6. (a) Current density – voltage characteristics of all-polymer blend bulk-heterojunction solar cells processed from different solvents: Chlorobenzene (CB), chloroform (CF) and o-Xylene (o-Xyl). (b) AFM height images of (upper row) PNDI-OR:PTB7 blend (CF) and o-Xylene (o-Xyl).

films and (lower row) PNDI-RO:PTB7 blend films, in which the scale bar is 1 μm . The number in each image is the rms roughness values of the corresponding blend film.

We prepared all-polymer bulk-heterojunction solar cells with all-polymer blend active layers consisting of PNDI-OR (or PNDI-RO) as an acceptor and poly({4,8-bis[(2-ethylhexyl)oxy]benzo-[1,2-b:4,5-b']dithiophene-2,6-diyl} {3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thio-phenediyl}) (PTB7) as a donor. PNDI-OR:PTB7 blend films processed using *o*-xylene as a solvent showed the highest power conversion efficiency (PCE) of 0.54% among the tested samples (see Table S3 for details). By contrast, lower PCE values were obtained with PNDI-RO:PTB7 blends (up to 0.13%), mainly due to these blends having much lower current density levels, despite the higher hole mobilities of PNDI-RO. We infer that the low current level of the PNDI-RO:PTB7 blends might originate from the large degree of phase separation, likely caused by the better crystalline ordering properties of PNDI-RO (Fig. S5b).^{S7} These results demonstrate the potential of using hybrid side chains as an alternative approach to control the phase separation and morphology of polymer-blend films in all-polymer solar cells.

Condition	Name	Crystallographic parameters	PNDI-OR	PNDI-RO
As-spun	lamella packing (100)	q (\AA^{-1})	0.290	0.219
		d-spacing (\AA)	21.7	28.6
		FWHM (\AA^{-1})	0.0647	0.0484
		Correlation length (\AA)	182.2	243.6
	π - π stack (010)	q (\AA^{-1})	1.581	1.601
		d-spacing (\AA)	4.0	3.9
		FWHM (\AA^{-1})	0.4205	0.1792
		Correlation length (\AA)	28.3	66.5
	backbone direction (001)	q (\AA^{-1})	0.383	0.389
		d-spacing (\AA)	16.4	16.2
		FWHM (\AA^{-1})	0.1791	0.0449
		Correlation length (\AA)	65.9	263.0
Thermally Annealed at 250 °C	lamella packing (100)	q (\AA^{-1})	0.239	0.223
		d-spacing (\AA)	26.3	28.1
		FWHM (\AA^{-1})	0.0334	0.0322
		Correlation length (\AA)	353.6	366.0
	π - π stack (010)	q (\AA^{-1})	1.581	1.625
		d-spacing (\AA)	4.0	3.9
		FWHM (\AA^{-1})	0.2220	0.1888
		Correlation length (\AA)	53.7	63.2
	backbone direction (001)	q (\AA^{-1})	0.386	0.385
		d-spacing (\AA)	16.3	16.3
		FWHM (\AA^{-1})	0.0358	0.0484
		Correlation length (\AA)	329.1	243.8

Table S1. Crystallographic information of PNDI-OR and PNDI-RO polymer thin films. The correlation length is determined from the fullwidth-at-half-maximum (FWHM) of X-ray diffraction using the Scherrer equation.^{S5}

Condition ^a		$\mu_{h,max}^b$ (cm ² /V·s)	$\mu_{h,avg}^c$ (cm ² /V·s)	V_T (V)	I_{on}/I_{off}
Polymer	T_{ann} (°C)				
PNDI-OR	As-spun ^d	0.006	0.005	6.0	~10 ⁴
	100	0.027	0.024	10.6	~10 ⁵
	150	0.043	0.037	15.5	~10 ⁵
	200	0.048	0.042	12.7	~10 ⁴
	250	0.091	0.088	9.7	~10 ⁵
	280	0.077	0.075	11.7	~10 ⁵
	Additive ^e	0.11	0.095	9.9	~10 ⁶
PNDI-RO	As-spun	0.062	0.055	15.6	~10 ⁶
	100	0.15	0.11	12.6	~10 ⁵
	150	0.32	0.25	15.4	~10 ⁵
	200	0.28	0.20	16.5	~10 ⁶
	250	0.43	0.32	12.7	~10 ⁷
	280	0.51	0.41	14.7	~10 ⁶
	Additive ^e	1.64	1.12	5.5	~10 ⁶

Table S2. PFET performance of the polymers. ^aThe n-channel characteristics of PFETs were measured with $V_D = 60$ V. ^bThe maximum mobility of the FET devices ($L = 150$ μm and $W = 1500$ μm). ^cThe average electron mobility of the FET devices. ^dThermal annealing was not applied. ^ePolymer films were processed with 1-chloronaphalene additive (1.2 v% with respect to a chloroform host solvent) and annealed at 250 °C or 280 °C.

Condition		J_{sc} (mA) ^b	V_{oc} (V) ^c	FF ^d	PCE (%) ^e
Polymer blends	Solvent / spin-casting rate (rpm) ^a				
PNDI-OR / PTB7	2-Chlorobenzene / 1500	1.90	0.74	0.304	0.43
	Chloroform / 4000	1.06	0.74	0.289	0.23
	o-Xylene / 2000	2.11	0.74	0.345	0.54
PNDI-RO / PTB7	1,2-Dichlorobenzene / 1000	0.39	0.74	0.398	0.11
	2-Chlorobenzene / 1500	0.34	0.74	0.273	0.07
	Chloroform / 4000	0.60	0.70	0.298	0.13
	o-Xylene / 2000	0.46	0.72	0.301	0.10

Table S3. Performance of all-polymer blend bulk-heterojunction solar cells. ^aThe processing solvents and optimum spin-casting rate. ^bShort-current density (J_{sc}). ^cOpen-circuit voltage (V_{oc}). ^dFill factor (FF). ^ePower conversion efficiency (PCE).

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