

Supporting Information

Morphology Evolution with Polymer Chain Propagation and Its Impacts on Device Performance and Stability of Non-fullerene Solar Cells

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1. Materials and characterizations

All reagents were purchased from commercial sources (Aldrich, Acros, and J&K, etc) and used as received without further purification unless specifically mentioned. Compound **1**, IT-4F, and Y6 were purchased from commercial sources. Anhydrous toluene was distilled in our lab.

Nuclear magnetic resonance (NMR): The ^1H and ^{13}C NMR were measured on a Bruker AV-500 MHz spectrometer with tetramethylsilane (TMS) as the internal reference.

Gel permeation chromatography (GPC): Molecular weights of the polymers were measured on an Agilent Technologies PL-GPC 220 high-temperature chromatograph in *ortho*-dichlorobenzene at 140 °C using a calibration curve of polystyrene standards.

Elemental analysis (EA): The EA data were acquired on a varioELcube elemental analyzer.

Thermogravimetric analysis (TGA): TGA measurements were carried out with a NETZSCH (TG209F3) apparatus at a heating rate of 20 °C min⁻¹ under a nitrogen atmosphere.

UV-vis absorption spectra: UV-vis absorption spectra of the polymers in chlorobenzene solutions and films were recorded on a SHIMADZU UV-3600 spectrophotometer. The solution concentration was 0.02 mg mL⁻¹, and the films were prepared by spin coating their solutions on glass substrates.

Square wave voltammetry (SWV): The SWV measurements were conducted on a CHI 600D electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M) in acetonitrile at a scan rate of 50 mV s⁻¹. A platinum electrode coated with the sample film, a platinum wire, and an Ag⁺/AgCl electrode was used as the working electrode, counter electrode, and reference electrode, respectively.

Atomic force microscopy (AFM): Tapping-mode AFM images were obtained on a Bruker Multimode 8 Microscope, the samples were cast on PEDOT:PSS-coated ITO substrates.

Transmission electron microscopy (TEM): TEM images were obtained using a JEM-2100F transmission electron microscope instrument operated at 200 kV, with the samples on top of copper grids.

X-ray scattering: GIWAXS measurements were performed at the SAXS/WAXS beamline of Australian Synchrotron. The X-ray energy was 12 keV, corresponding to a wavelength of 1.03 Å. The incidence angle was set to be 0.16°. The sample-to-detector distance (SDD) was 690 mm, which was calibrated with silver behenate. The relative scattering intensity was recorded with a Pilatus2M detector. The samples were prepared on silicon substrates with the same conditions as the device preparation. GIWAXS performed at the ALS are described as follows. The samples were measured in a helium environment to minimize air scattering using 10 keV energy X-rays, which was incident at a grazing angle of 0.13°. The scattered X-rays were

detected using a Pilatus 2M detector. The sample to detector distance was 280 mm, which is calibrated by Silver-Behenate. RSoXS measurements were performed at the beamline 11.0.1.2 at ALS by following reported protocols. Data analysis was performed using the NIKA package.

Contact angle measurements: The contact angle tests were conducted on a Dataphysics OCA40 Micro surface contact angle analyzer. The surface tension of the materials was characterized and calculated by the contact angles of the water and ethylene glycol via the Owens-Wendt & Kaelble (OW) method, where γ^d and γ^p are the dispersion and polarity components, respectively. The samples were cast on PEDOT:PSS-coated ITO substrates, and the contact angle images were taken when the liquids had been dropped on the sample films for 60 seconds.

2. Device fabrication and characterization

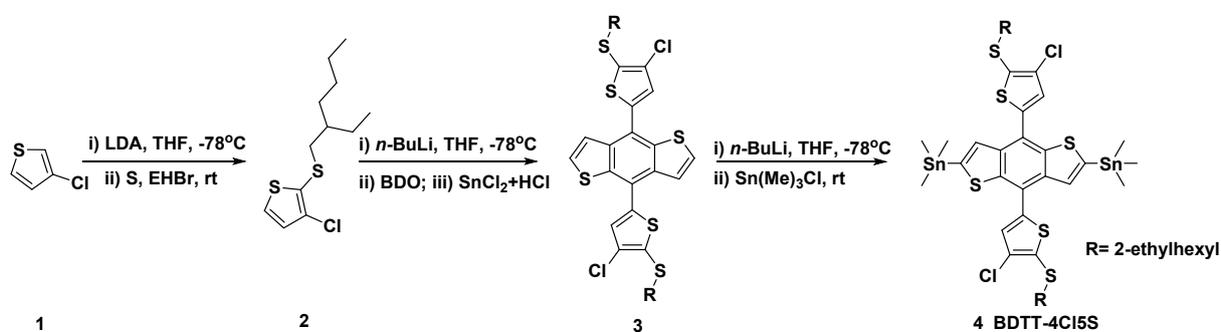
Fabrication of polymer solar cells: ITO-coated glass substrates were successively pre-cleaned with isopropanol, detergent, de-ionized water, and isopropanol. About 40 nm PEDOT: PSS (Clevios P VP AI4083) was spin-coated onto the plasma-treated ITO substrates and baked at 150 °C for 15 min. After that, the substrates were transferred into a nitrogen protected glove box. The different active layers were formed by spin coating from their solutions with the mixed solvents of chloroform (CF)/1-chloronaphthalene (CN) (99.2:0.8, v/v) for P-17k and P-30k, and chlorobenzene (CB)/1-chloronaphthalene (CN) (99.2:0.8, v/v) for P-53k and P-98k, affording films with thicknesses of 95–100 nm. It is worth pointing out that P-98k:Y6 films were cast from hot solution (70–80 °C). After removal of the additive by vacuum, the active layer was thermal-annealed at 110 °C for 10 minutes. Then 5 nm PNDIT-F3N-Br was spin-coated onto the active layers. The device fabrication was finished by evaporating 100 nm Ag through a shadow mask in a vacuum chamber with a base pressure of 1×10^{-7} mbar.

Current density–voltage ($J-V$) characteristics: The $J-V$ curves were measured on a computer-controlled Keithley 2400 source meter under 1 sun, AM1.5 G spectra from the solar simulator (Enlitech, Taiwan), the light intensity was 100 mW cm^{-2} as calibrated by using a China General Certification Centre (CGC) certified reference monocrystal silicon cell (Enlitech), and the irradiation area of the solar simulator was $12 \times 12 \text{ cm}^2$. Before the $J-V$ test of small area devices, a physical mask containing an aperture with a precise area of 4 mm^2 was used to define the device area.

External quantum efficiencies (EQEs): EQEs were recorded on a commercial EQE measurement system (Enlitech, QE-R3011, Taiwan).

Single-carrier devices: Hole and electron mobilities were acquired from the hole-only devices with a configuration of ITO/PEDOT:PSS (40 nm)/polymer:Y6/MoO₃ (10 nm)/Ag (100 nm) and electron-only devices with a configuration of ITO/ZnO (40 nm)/polymer:Y6/Ca (10 nm)/Al (100 nm), respectively. The dark current densities of the polymer:Y6 blends were measured by applying a voltage between 0 and 5 V using a computer-controlled Keithley 2400 source meter under an N₂ atmosphere. The data were analyzed according to the Mott–Gurney law that considers a Poole–Frenkel-type dependence of mobility on the electric field, given by $J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \frac{V^2}{d^3} \exp(0.89 \gamma \sqrt{\frac{V}{d}})$, where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer which is assumed to be 3 for organic semiconductors, μ_0 is the zero-field mobility, V is the voltage drop across the device, d is the film thickness of the active layer, and γ is a parameter that describes the strength of the field-dependence effect. The applied voltage is used without correcting for series resistance or built-in voltage, which offers the best fitting of the experimental data following the protocol reported in the literature.¹ The hole and electron mobilities are extracted with the fit parameters at an electric field (E) of 1×10^5 V cm⁻¹ by the Murgatroyd equation $\mu = \mu_0 \exp(\gamma \sqrt{E})$.

3. Synthetic procedures and characterizations



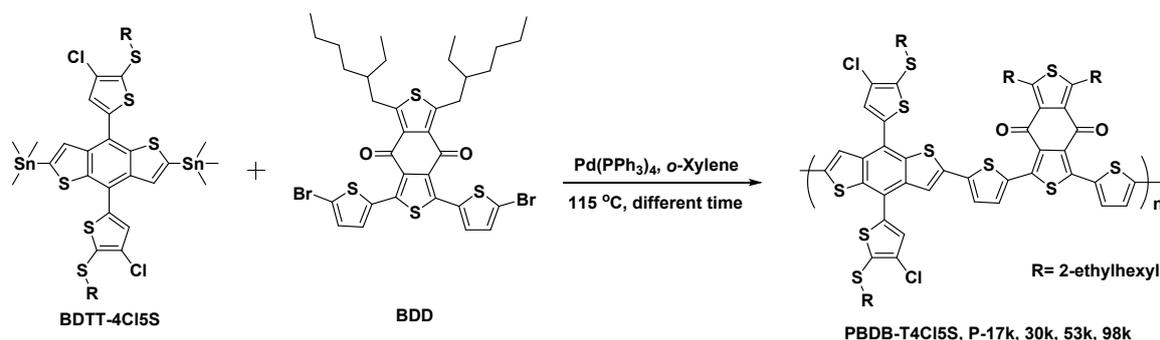
Synthesis of compound 2 (3-chloro-2-((2-ethylhexyl)thio)thiophene): Compound **1** (2.37 g, 20 mmol) was added into a 100 mL three-necked bottle under argon protection. After being purged by argon twice, anhydrous tetrahydrofuran (THF, 40 mL) was added and then the solution cooled to -78 °C under argon protection. 20 mL of lithium diisopropylamide (LDA) solution (20 mmol, 1.0 M in THF/hexanes) was added dropwise at -78 °C. Then, the reaction was warmed up to 0 °C and stirred for 1 hour. Sulfur powder (0.64 g, 20 mmol) was quickly added to the reaction mixture by one portion and the reaction was kept at 0 °C for 2 hours. Subsequently, 2-ethylhexyl bromide (3.86g, 20 mmol) was added, and then the reaction mixture was warmed to room temperature and stirred overnight. Finally, the reaction mixture was

poured into water and extracted with dichloromethane. The organic layer was dried over MgSO₄. After the removal of solvents, the crude product was purified by column chromatography of silica gel using PE as the eluent and then further purified by distillation to afford compound **2** as a colorless oil (4.00 g, yield 76%). ¹H NMR (500 MHz, CDCl₃): δ = 7.26 (d, *J*=2.0, 1H), 6.94 (d, *J*=5.6, 1H), 2.82 (dd, *J*=6.0, 0.8, 2H), 1.49 – 1.22 (m, 9H), 0.90 – 0.84 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): δ = 130.09, 129.44, 128.25, 127.13, 42.06, 39.04, 32.05, 28.71, 25.29, 22.92, 14.08, 10.70.

Synthesis of compound 3 (*4,8-bis(4-chloro-5-((2-ethylhexyl)thio)thiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene*): Compound **2** (3.94 g, 15 mmol) was added into a 100 mL three-necked bottle under argon protection. After being purged by argon twice, anhydrous tetrahydrofuran (THF, 20 mL) was added and then the solution was cooled to –78 °C under argon protection. 6 mL of *n*-butyllithium (*n*-BuLi, 15 mmol, 2.5 M in hexane) solution was added dropwise at –78 °C, then the reaction was warmed up to 50 °C and stirred for 2 hours. Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (BDO, 1.10 g, 5 mmol) was quickly added to the reaction mixture by one portion at room temperature and the reaction system was kept at 50 °C for 2 hours. Subsequently, A mixture of SnCl₂·2H₂O (6.78g, 30 mmol) in 10% HCl (10 mL) was added into the reaction at room temperature, and then the reaction mixture was stirred overnight at 50 °C. Finally, the reaction mixture was poured into water and extracted with dichloromethane. The organic layer was dried over MgSO₄. After the removal of solvents, the crude product was purified by column chromatography of silica gel using petroleum ether as the eluent and then further purified by preparation GPC to afford compound **3** as a light yellow viscous oil (3.03 g, yield 85%). ¹H NMR (500 MHz, CDCl₃): δ 7.59 (d, *J* = 5.7 Hz, 2H), 7.52 (d, *J* = 5.7 Hz, 2H), 7.31 (s, 2H), 2.96 (dd, *J* = 6.2, 2.3 Hz, 4H), 1.62 (m, 2H), 1.48 – 1.20 (m, 16H), 0.93 – 0.89 (m, 12H). ¹³C NMR (125 MHz, CDCl₃): δ = 140.32, 139.00, 136.49, 131.04, 129.73, 128.74, 128.44, 122.99, 122.78, 42.06, 39.29, 32.17, 28.82, 25.42, 22.94, 14.14, 10.82. **MS (MALDI-TOF)**: Calcd for C₃₄H₄₀Cl₂S₆: 710.08. Found: 710.10.

Synthesis of compound 4 (*(4,8-bis(4-chloro-5-((2-ethylhexyl)thio)thiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane)*): Compound **3** (710 mg, 1 mmol) was added into a 50 mL two-necked bottle under argon protection. After being purged by argon twice, anhydrous tetrahydrofuran (THF, 20 mL) was added and then the solution was cooled to –78 °C under argon protection. 1.2 mL of *n*-butyllithium (3 mmol, 2.5 M in hexane) was added dropwise. Then the reaction mixture was warmed to –35 °C and stirred for 2 h. Subsequently, 4 mL of trimethylstannane chloride (4.0 mmol, 1.0 M in THF) was added to the reaction mixture at –35 °C. And then the reaction mixture was warmed to room temperature and stirred

overnight. After that, the reaction mixture was poured into water and extracted with hexane. The organic layer was dried over MgSO_4 . After the removal of the solvent, the crude product was purified by recrystallization using ethanol to obtain the target compound **4** as a yellow solid (700 mg, 67%). $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ): 7.60 (s, 2H), 7.32 (s, 2H), 2.96 (dd, $J = 6.2$, 0.7 Hz, 4H), 1.67 – 1.58 (m, 2H), 1.52 – 1.21 (m, 16H), 0.94 – 0.92 (m, 12H), 0.42 (s, 18H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3 , δ): 143.91, 141.25, 137.28, 130.46, 130.24, 129.74, 128.53, 121.22, 42.04, 39.29, 32.15, 28.79, 25.41, 22.93, 14.14, 10.86, -8.25. **MS (MALDI-TOF)**: Calcd for $\text{C}_{40}\text{H}_{56}\text{Cl}_2\text{S}_6\text{Sn}_2$: 1037.57. Found: 1038.01.



Polymerization of P-17k: In the degassed solution of compound **4** (106.7 mg, 0.103 mmol) and monomer BDD (76.7 mg, 0.1 mmol) in *o*-xylene (4 mL), $\text{Pd(PPh}_3)_4$ (6.9 mg, 0.006 mmol) was added under argon protection. Then the mixture was stirred at 110 °C for 16 hours. After that, 2-(tributylstannyl)thiophene and 2-bromothiophene were sequentially added to the reaction with 2 hours interval. After another 2 hours, the reaction mixture was diluted with chlorobenzene and refluxed with an aqueous solution of sodium *N,N*-diethylcarbamidithioate trihydrate for 2 hours. After cooling to room temperature, the reaction mixture was precipitated in methanol and filtered through a Soxhlet thimble. The precipitate was subjected to Soxhlet extraction with methanol, acetone, hexane, dichloromethane, chloroform sequentially under argon protection. The chloroform fraction was concentrated under reduced pressure and precipitated into methanol, and the precipitate was dried under vacuum to obtain **P-17k** (106 mg, yield = 80%). $\bar{M}_n = 17 \text{ kg mol}^{-1}$, $D_M = 2.6$. Elemental analysis (EA) calcd, C: 61.93%, H: 5.96%, S: 24.31%. Found, C: 61.59%, H: 5.74%, S: 23.97%.

Polymerization of P-30k, 53k, and 98k: In the degassed solution of compound **4** (103.8 mg, 0.1 mmol) and monomer BDD (76.7 mg, 0.1 mmol) in *o*-xylene (4 mL) was prepared under argon protection, $\text{Pd(PPh}_3)_4$ (4.6 mg, 0.004 mmol) was added. Then the mixture was stirred at 110 °C for 11, 16, and 24 hours to get P-30k, P-53k, and P-98k, respectively. After that, 2-(tributylstannyl)thiophene and 2-bromothiophene were sequentially added to the reaction with

2 hours interval. After another 2 hours, the reaction mixture was diluted with chlorobenzene and refluxed with an aqueous solution of sodium *N,N*-diethylcarbamodithioate trihydrate for 2 hours. After cooling to room temperature, the reaction mixture was precipitated in methanol and filtered through a Soxhlet thimble. The precipitate was subjected to Soxhlet extraction with methanol, acetone, hexane, dichloromethane, chloroform sequentially under argon protection. The chloroform or chlorobenzene fractions were concentrated under reduced pressure and precipitated into methanol, and the precipitates were dried under vacuum to obtain resulting polymers.

P-30k (CF fraction, yield = 93%). $\bar{M}_n = 30 \text{ kg mol}^{-1}$, $D_M = 1.9$. Elemental analysis (EA) calcd, C: 61.93%, H: 5.96%, S: 24.31%. Found, C: 61.81%, H: 5.80%, S: 24.29%.

P-53k (CB fraction, yield = 91%). $\bar{M}_n = 53 \text{ kg mol}^{-1}$, $D_M = 1.6$. Elemental analysis (EA) calcd, C: 61.93%, H: 5.96%, S: 24.31%. Found, C: 62.08%, H: 5.83%, S: 24.07%.

P-98k (CB fraction, yield = 76%). $\bar{M}_n = 98 \text{ kg mol}^{-1}$, $D_M = 1.4$. Elemental analysis (EA) calcd, C: 61.93%, H: 5.96%, S: 24.31%. Found, C: 62.03%, H: 5.80%, S: 24.20%.

4. Additional figures and tables

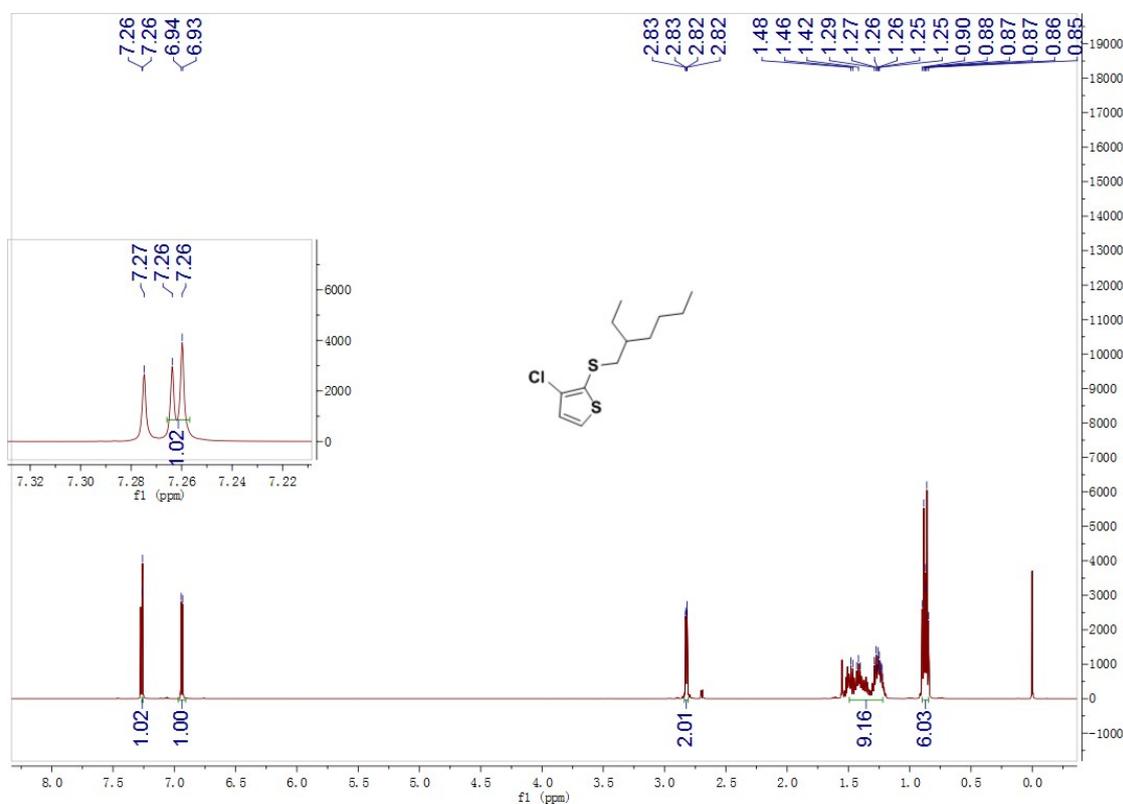


Figure S1. The ¹H NMR spectrum of compound **2** in CDCl₃.

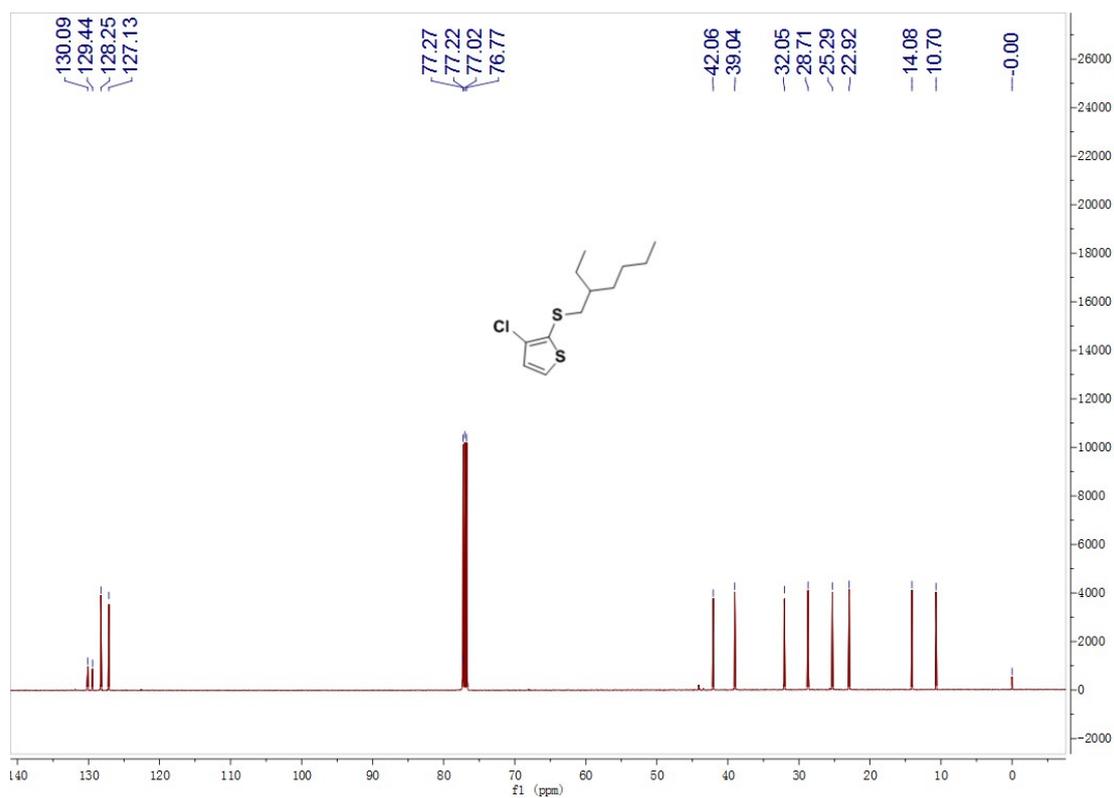


Figure S2. The ^{13}C NMR spectrum of compound **2** in CDCl_3 .

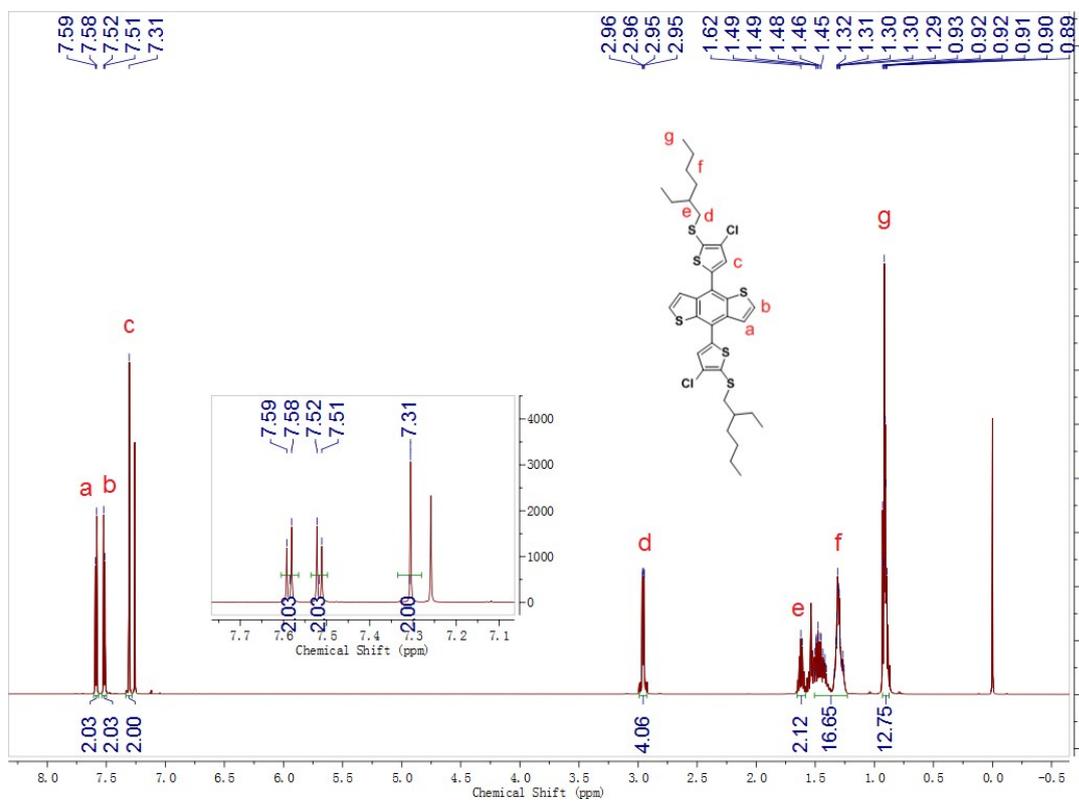


Figure S3. The ^1H NMR spectrum of compound **3** in CDCl_3 .

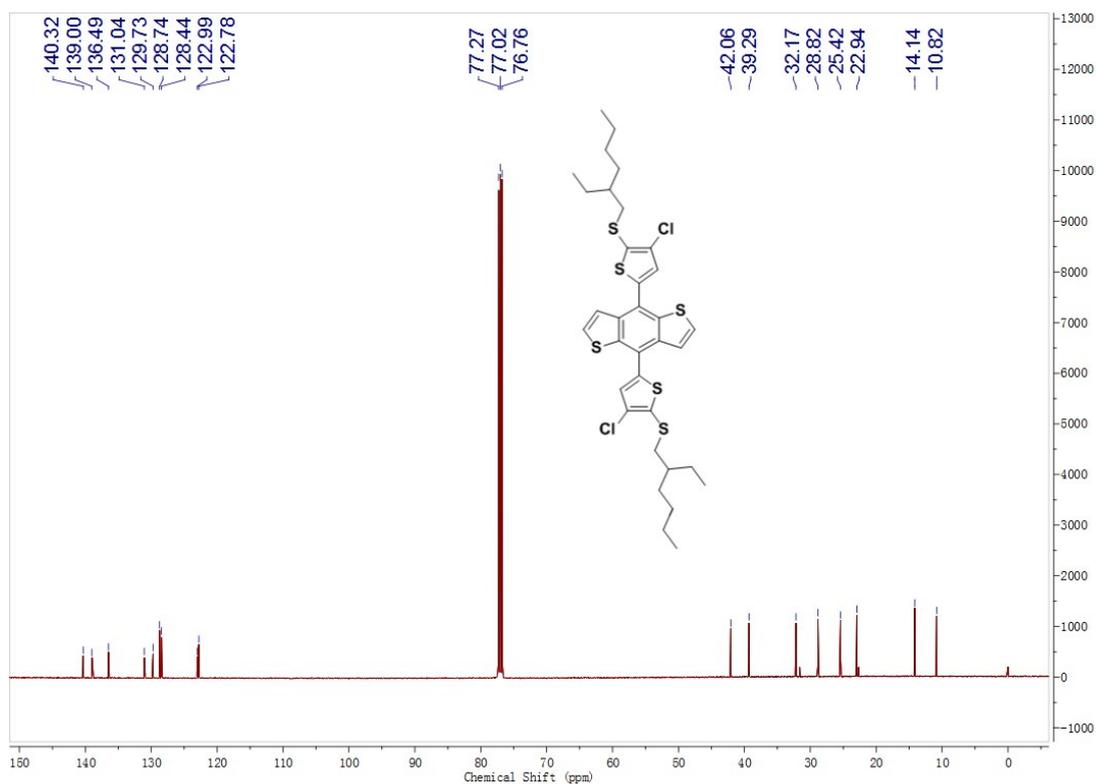


Figure S4. The ^{13}C NMR spectrum of compound **3** in CDCl_3 .

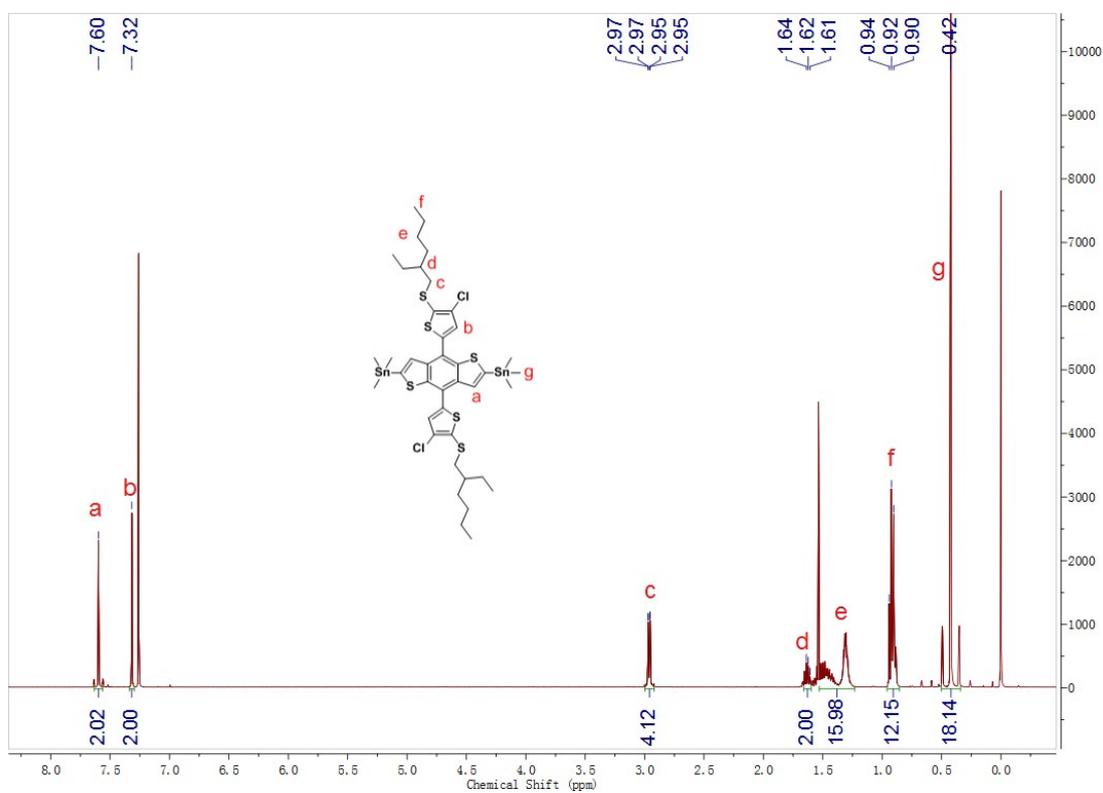


Figure S5. The ^1H NMR spectrum of compound **4** in CDCl_3 .

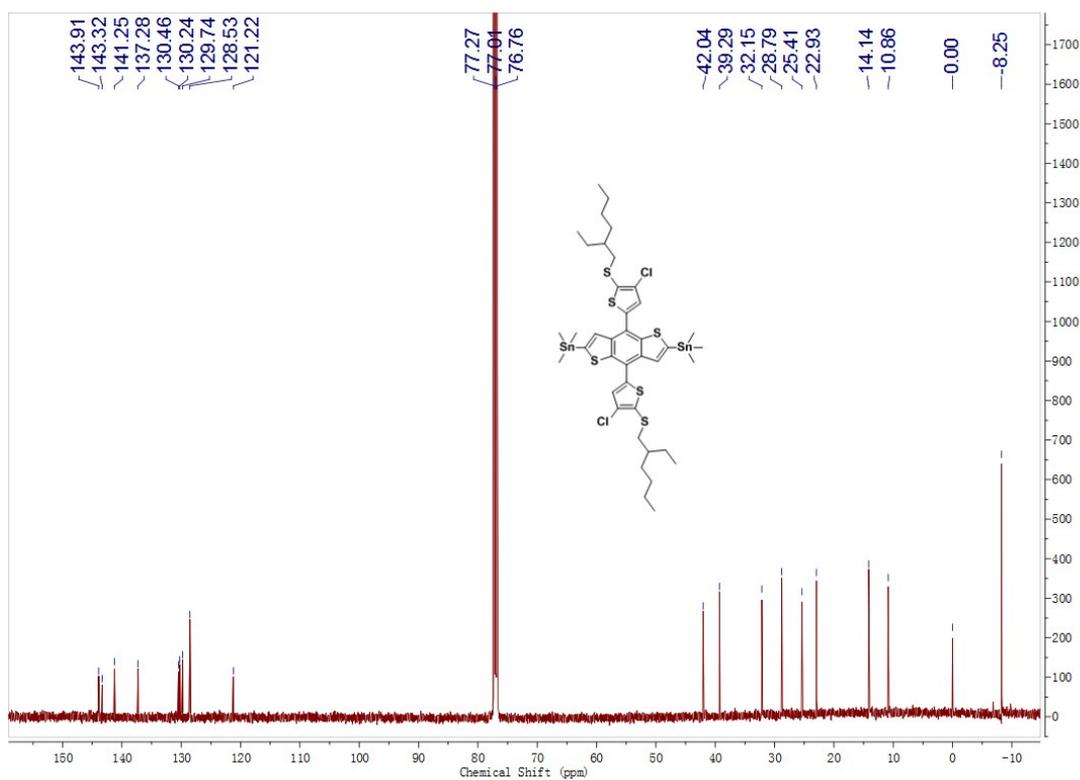


Figure S6. The ^{13}C NMR spectrum of compound **4** in CDCl_3 .

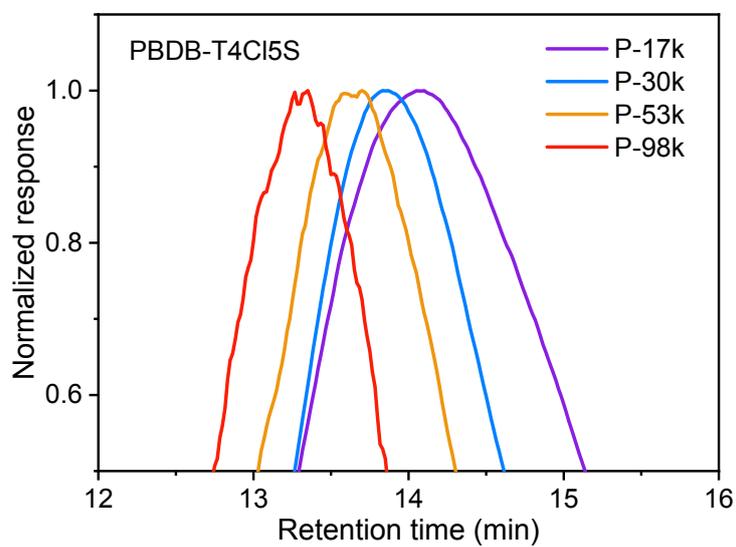


Figure S7. The GPC traces of P-17k, P-30, P-53k, and P-98k with *o*-DCB as the eluent at 140 $^{\circ}\text{C}$.

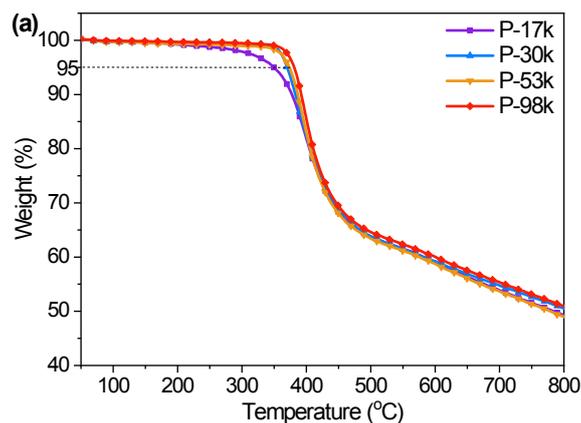


Figure S8. The thermogravimetric thermograms of the polymers.

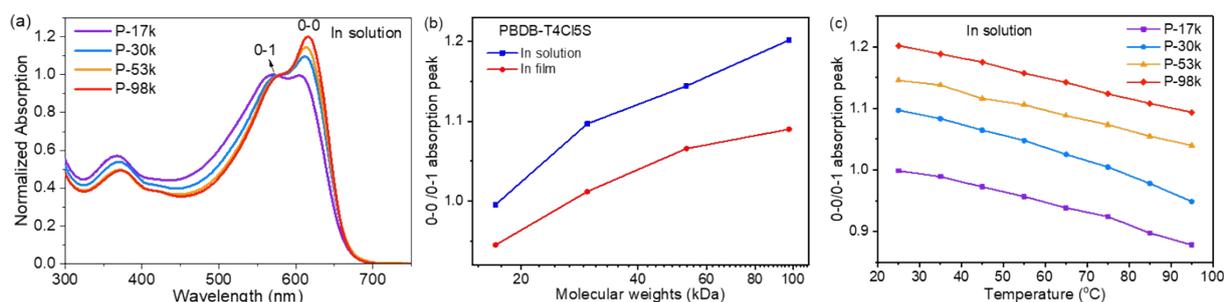


Figure S9. (a) The absorption spectra of the polymers in CB solutions, (b) the plots of relative aggregation degrees with polymer molecular weights, and (c) the plots of relative aggregation degrees versus solution temperature.

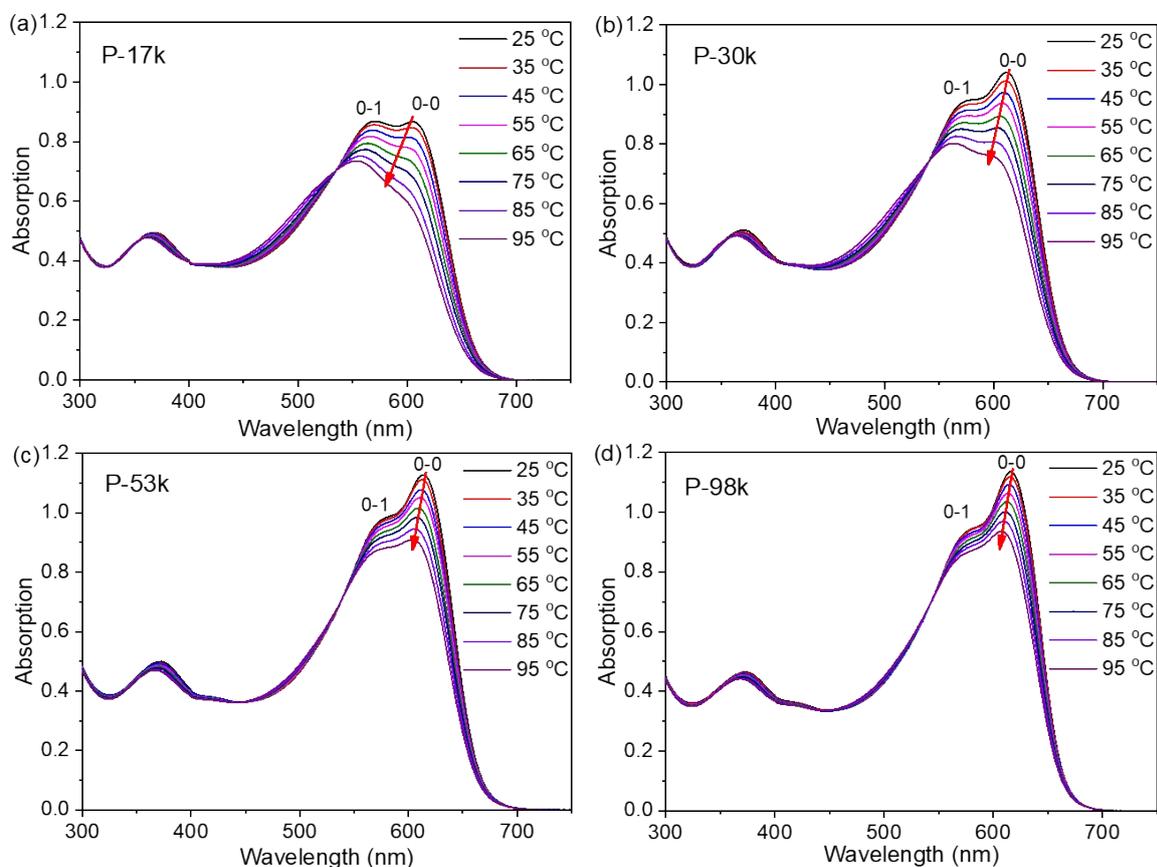


Figure S10. Temperature-dependent absorption spectra of (a) P-17k, (b) P-30k, P-53k, and P-98k in dilute CB solutions, respectively.

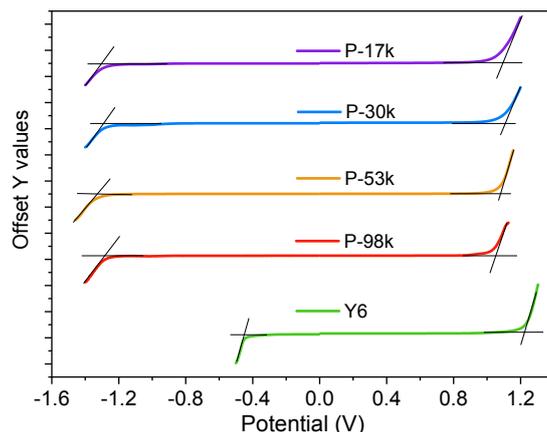


Figure S11. Square wave voltammograms of the polymers and Y6.

Table S1. Electrochemical properties and energy levels of the polymers and Y6.

Polymer	E_{red} [V] ^a	E_{ox} [V] ^a	E_{LUMO} [eV] ^b	E_{HOMO} [eV] ^b
P-17k	-1.30	1.10	-3.20	-5.60
P-30k	-1.29	1.09	-3.21	-5.59
P-53k	-1.31	1.08	-3.20	-5.58
P-98k	-1.29	1.06	-3.21	-5.56
Y6	-0.43	1.23	-4.07	-5.73

a) Versus Fc/Fc⁺; b) $E_{\text{HOMO}} = -(E_{\text{ox}} + 5.13 - E_{\text{Fc/Fc}^+})$ eV, $E_{\text{LUMO}} = -(E_{\text{red}} + 5.13 - E_{\text{Fc/Fc}^+})$ eV, $E_{\text{Fc/Fc}^+} = 0.63$ V;

Table S2. GIWAXS data of the polymer:Y6 blended films.

Polymers	OOP (010) peak [\AA^{-1}]	OOP (010) distance [\AA]	OOP (010) FWHM/CL [nm]	IP (100) peak [\AA^{-1}]	IP (100) distance [\AA]
P-17k	1.79	3.51	0.19/3.0	0.31	20.3
P-30k	1.80	3.49	0.22/2.6	0.29	21.6
P-53k	1.80	3.49	0.19/3.0	0.30	20.9
P-98k	1.81	3.47	0.20/2.8	0.29	21.6

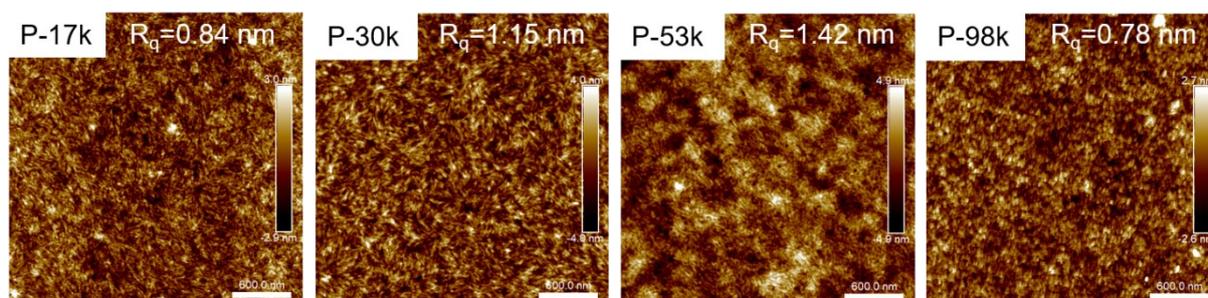


Figure S12. AFM surface images of the neat polymer films (scale bar 600 nm).

Table S3. Device parameters of the PSCs based on polymer:Y6 blends fabricated with CB solvent under AM1.5G illumination (100 mW cm^{-2}).^a

Polymer	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]
P-17k	0.83 (0.84 \pm 0.01)	19.0 (18.0 \pm 0.8)	0.55 (0.56 \pm 0.01)	8.7 (8.4 \pm 0.3)
P-30k	0.84 (0.83 \pm 0.01)	21.4 (20.8 \pm 0.5)	0.68 (0.68 \pm 0.01)	12.2 (11.8 \pm 0.4)
P-53k	0.84 (0.84 \pm 0.01)	25.6 (25.3 \pm 0.3)	0.76 (0.75 \pm 0.01)	16.3 (15.9 \pm 0.3)
P-98k	0.82 (0.82 \pm 0.01)	25.9 (25.8 \pm 0.4)	0.76 (0.76 \pm 0.01)	16.2 (16.0 \pm 0.2)

a) The data in brackets are the average values and standard deviations of at least 8 independent devices for each blend.

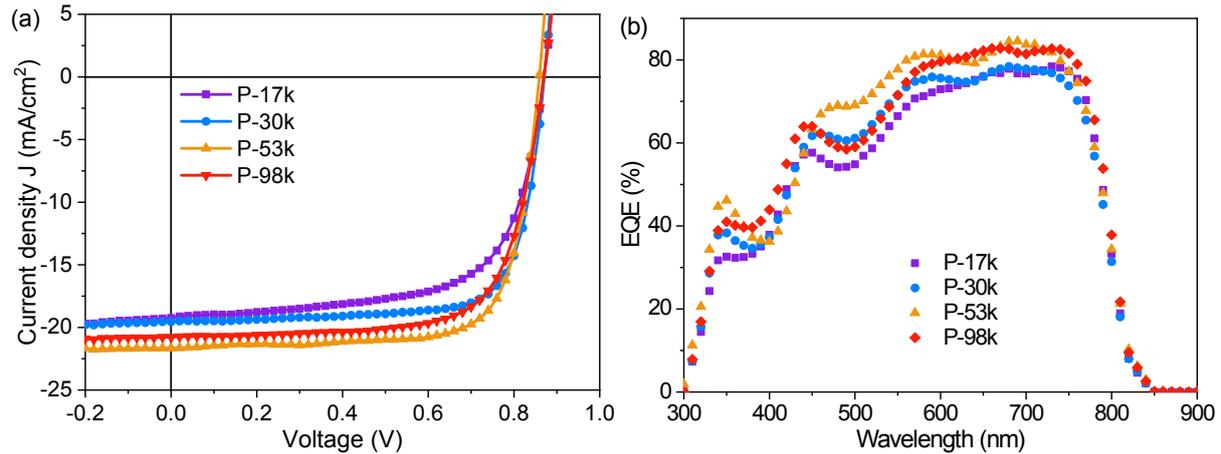


Figure S13. (a) J - V curves and (b) EQE spectra of the PSCs based on polymer:IT-4F blends.

Table S4. Device parameters of the PSCs based on polymer:IT-4F blends under AM1.5G illumination (100 mW cm^{-2}).^a

Polymer	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]
P-17k	0.87 (0.87 \pm 0.01)	19.3 (19.6 \pm 0.7)	0.66 (0.63 \pm 0.02)	11.0 (10.8 \pm 0.2)
P-30k	0.87 (0.87 \pm 0.01)	19.5 (19.8 \pm 0.2)	0.75 (0.74 \pm 0.01)	12.8 (12.7 \pm 0.1)
P-53k	0.86 (0.86 \pm 0.01)	21.7 (21.2 \pm 0.3)	0.75 (0.75 \pm 0.01)	13.9 (13.6 \pm 0.2)
P-98k	0.87 (0.87 \pm 0.01)	20.8 (20.7 \pm 0.1)	0.71 (0.71 \pm 0.01)	12.9 (12.8 \pm 0.1)

a) The data in brackets are the average values and standard deviations of at least 10 independent devices for each blend.

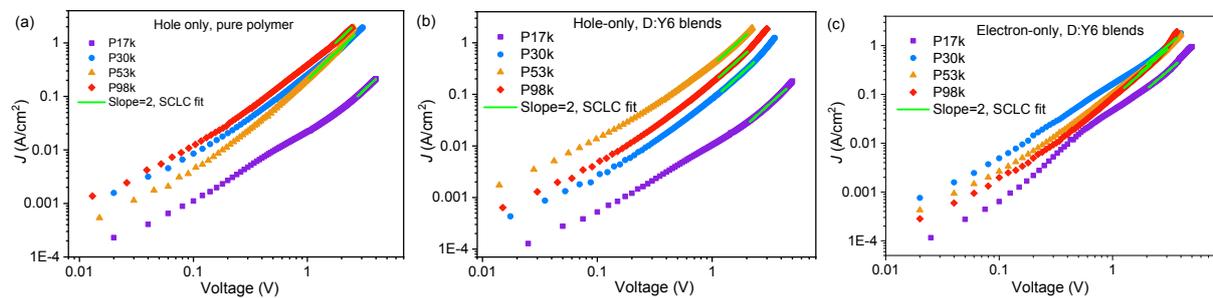


Figure S14. J - V characteristics of (a) hole-only devices with a configuration of ITO/PEDOT:PSS/polymer/MoO₃/Ag, (b) hole-only devices with a configuration of ITO/PEDOT:PSS/polymer:Y6/MoO₃/Ag and (c) electron-only devices with a configuration of ITO/ZnO/polymer:Y6/Ca/Al plotted in dual logarithmic coordinates.

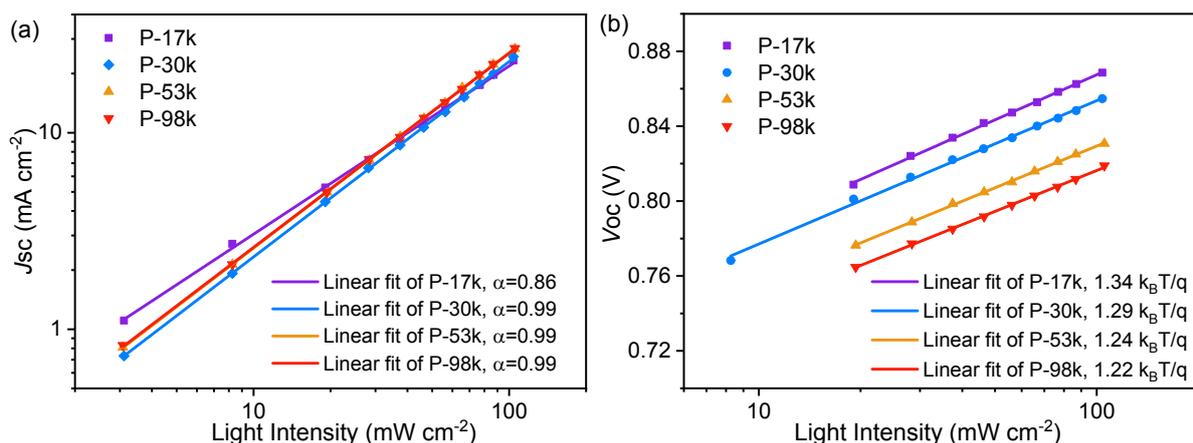


Figure S15. (a) J_{sc} and (b) V_{oc} as a function of P_{light} of the polymer:Y6 solar cells.

Table S5. Electrical properties of the PSCs and charge carrier mobilities acquired from single-carrier devices based on polymer:Y6 blends.

Polymers	V_0 [V]	J_{sat} [mA cm^{-2}]	$P[E, T]$	μ_h [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	μ_e [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	μ_e/μ_h
P-17k	0.93	27.8	82.0%	$(2.6 \pm 0.2) \times 10^{-5}$	$(5.6 \pm 0.1) \times 10^{-5}$	2.15
P-30k	0.91	24.3	94.8%	$(2.8 \pm 0.1) \times 10^{-4}$	$(2.7 \pm 0.5) \times 10^{-4}$	0.96
P-53k	0.89	26.8	96.3%	$(3.6 \pm 0.8) \times 10^{-4}$	$(3.7 \pm 0.2) \times 10^{-4}$	1.03
P-98k	0.87	26.6	97.1%	$(5.4 \pm 0.5) \times 10^{-4}$	$(5.2 \pm 0.6) \times 10^{-4}$	0.96

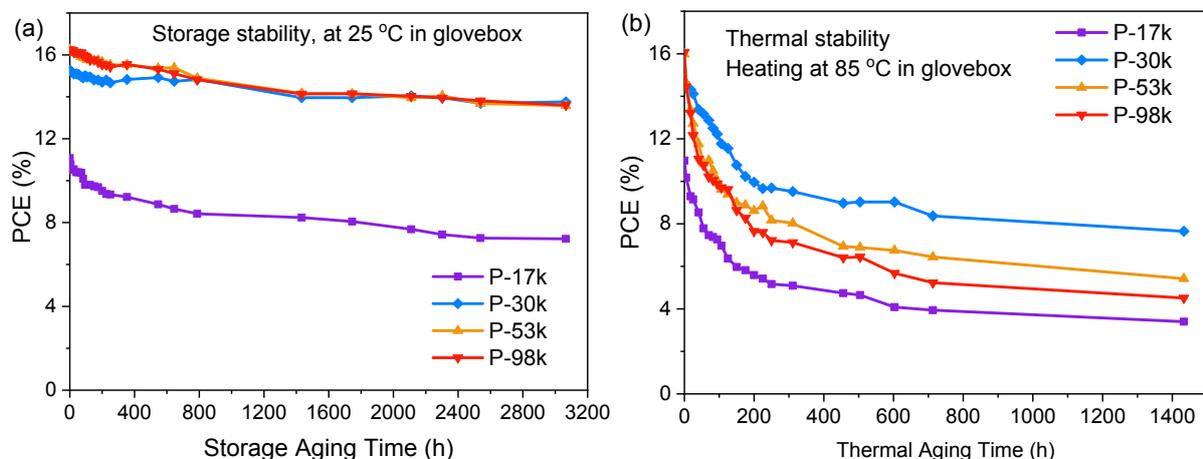


Figure S16. Device performance of the PSCs based on the polymer:Y6 blends with the storage time (a) and over 85 °C aging time (b).

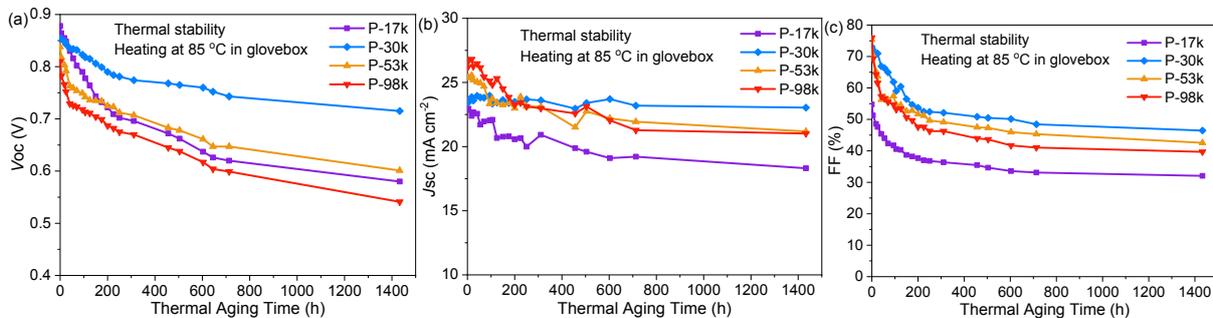


Figure S17. Device parameters of the PSCs based on the polymer:Y6 blends over 85 °C aging time: (a) V_{oc} , (b) J_{sc} , and (c) FF.

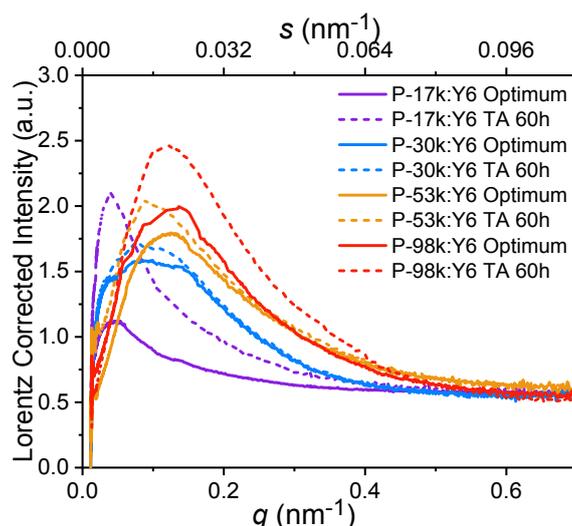
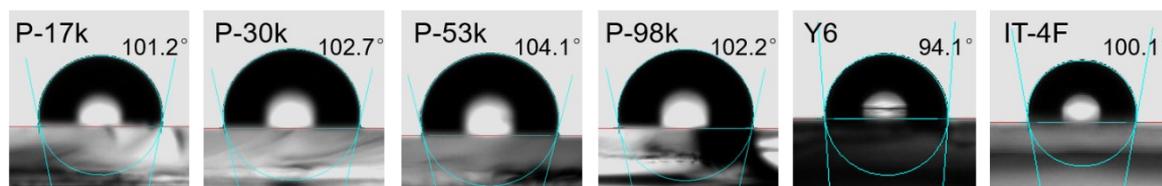


Figure S18. RSoXS profiles of the freshly cast polymer:Y6 blended films (Optimum) and the films that continuously heated at 85 °C for 60 hours (TA 60 h).

Table S6. RSoXS data of the polymer:Y6 fresh films and the blended films after 85 °C aging for 60 hours.

Sample Layers	q [nm ⁻¹]	Long period [nm]	Integrated Scattering Intensity (ISI)	\sqrt{ISI}	Relative domain purity
P-17k:Y6 (fresh)	0.046	137	0.462	0.686	0.80
P-30k:Y6 (fresh)	0.099	64	0.588	0.767	0.90
P-53k:Y6 (fresh)	0.126	50	0.681	0.825	0.96
P-98k:Y6 (fresh)	0.136	46	0.731	0.855	1.00
P-17k:Y6 (TA 60 h)	0.040	157	0.601	0.775	0.91
P-30k:Y6 (TA 60 h)	0.078	80	0.630	0.794	0.93
P-53k:Y6 (TA 60 h)	0.088	72	0.761	0.872	1.02
P-98k:Y6 (TA 60 h)	0.120	52	0.807	0.898	1.05

(a) Water



(b) Ethylene glycol

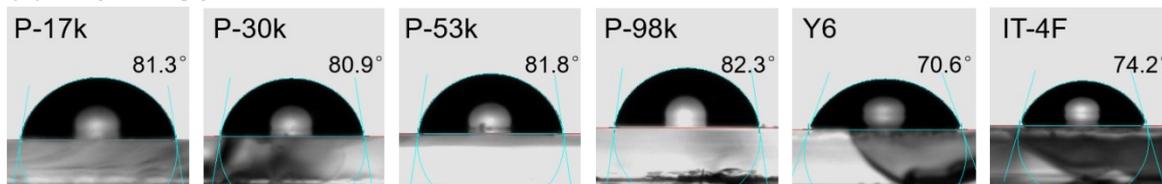
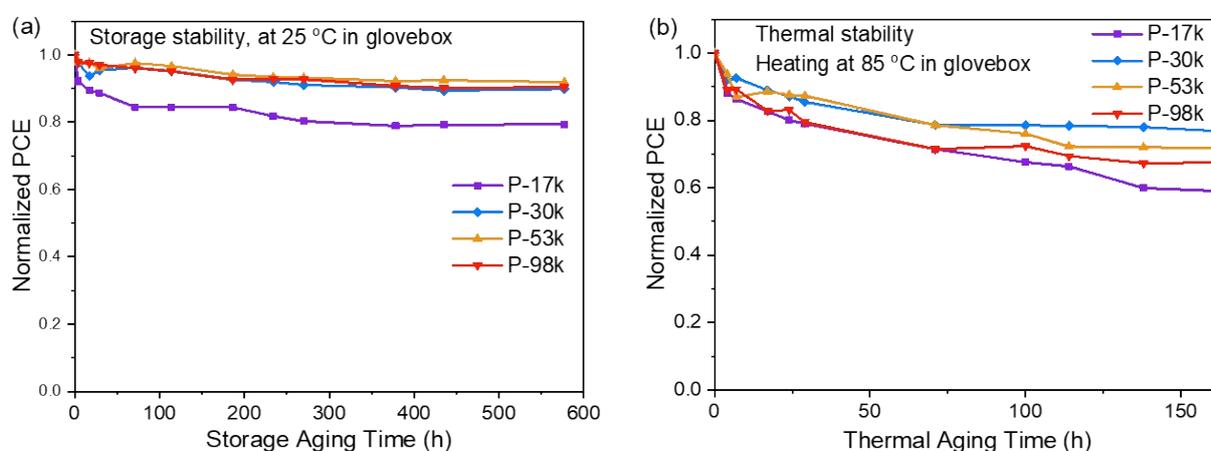


Figure S19. Contact angles of water (a) and ethylene glycol (b) on the neat films of PBDB-T4Cl5S polymers, Y6, and IT-4F.

Table S7. Contact angles, surface energy parameters of the films, and relative χ

Material	Contact angle		γ^d [mN/m] ^b	γ^p [mN/m] ^b	γ [mN/m]	Relative χ^c	
	[Water] [°]	[EG] ^a [°]				(with Y6)	(IT-4F)
P-17k	101.1±0.3	81.3±0.6	14.50	2.68	17.18	0.46 <i>K</i>	0.62 <i>K</i>
P-30k	102.7±0.1	80.7±0.4	17.30	1.58	18.88	0.23 <i>K</i>	0.34 <i>K</i>
P-53k	104.2±0.2	81.8±0.4	17.54	1.25	18.79	0.24 <i>K</i>	0.36 <i>K</i>
P-98k	102.6±0.3	82.2±0.3	15.24	2.05	17.30	0.44 <i>K</i>	0.60 <i>K</i>
Y6	93.8±0.5	70.8±0.2	20.02	3.27	23.28	--	--
IT-4F	100.1±0.4	74.2±0.3	23.21	1.11	24.32	--	--

a) EG represents the contact angle of ethylene glycol; b) γ^d and γ^p represent the dispersion and polarity components of surface tensions, respectively; c) Estimates for the Flory–Huggins interaction parameter ($\chi_{\text{donor-acceptor}}$) using the empirical relation $\chi = K(\sqrt{\gamma_D} - \sqrt{\gamma_A})^2$.

**Figure S20.** Device stability based on the polymer: IT-4F blends with the storage (a) and thermal (b) aging time.

References

1. J. C. Blakesley, F. A. Castro, W. Kylberg, G. F. A. Dibb, C. Arantes, R. Valaski, M. Cremona, J. S. Kim and J. S. Kim, *Org. Electron.*, 2014, **15**, 1263-1272.