Supporting Information

Impact of Side Chain Placement on Thermal Stability of Solar Cells in Thiophene–Thiazolothiazole Polymers

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Materials.

4-Alkylthiophene-2-carbaldehyde (**1a** and **1b**),[S1] 2,5-bis(3-(2-butyloctyl-5-(trimethylstannyl) thiophen-2-yl)thiazolo[5,4-*d*]thiazole (**4**),[S2] PTzBT-BOBO,[S2] and PTzBT-BOHD[S2] were synthesized according to the reported procedure. All chemicals were used as purchased. Toluene was purified by a Glass Contour Solvent System (Nikko Hanssen & Co., Ltd.). Polymerization was carried out with a microwave reactor (Biotage Initiator). Nuclear magnetic resonance (NMR) spectra were obtained in deuterated chloroform and *o*-dichlorobenzene (DCB) with TMS as internal reference by using a JNM-ECS400 (JEOL RESONANCE). High-resolution mass spectra (HR-MS) were obtained with a GCMS-QP-2010SE spectrometer (SHIMADZU) using an electron impact ionization procedure (70 eV). Molecular weights were determined by gel permeation chromatography (GPC) by calibrating with polystyrene standards using a TOSOH HLC-8121GPC/HT at 140 °C with DCB as the solvent.

Synthesis.

*2,5-Bis(4-(2-butyloctyl)thiophen-2-yl)thiazolo[5,4-d] thiazole (**2a**).*

Dithiooxamide (1.8 g, 15 mmol) and 3-((2-butyloctyl)thiophene-2-carbaldehyde (**1a**) (9.0 g, 32 mmol) were mixed in a round-bottom flask and heated at 200 °C for 12 h. The crude product was purified by column chromatography on silica gel (20% ethyl acetate in hexane), and followed by recrystallization from hexane:ethanol = 1:2, which gave the pure product as yellow powder (2.8 g, 31%). HR-MS Calcd for $C_{36}H_{54}N_2S_4$ $[M+H]^+$: 643.32481. Found: 643.32487. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 2H), 7.02 (s, 2H), 2.55 (d, $J = 7.2$ Hz, 4H), 1.70–1.60 (m, 2H), 1.40–1.20 (m, 24H), 0.86 (t, $J = 7.0$ Hz, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.9, 149.8, 143.6, 137.1, 128.6, 124.5, 39.0, 35.1, 33.4, 33.1, 32.0, 29.8, 28.9, 26.7, 23.2,22.8,14.29, 14.28.

*2,5-Bis(4-(2-hexyldecyl)thiophen-2-yl)thiazolo[5,4-d]thiazole (**2b**).*

Dithiooxamide (1.5 g, 12.5 mmol) and 3-((2-hexyldecyl)thiophene-2-carbaldehyde (**1b**) (9.0 g, 27 mmol) were mixed in a round-bottom flask and heated at 200 °C for 12 h. The crude product was purified by column chromatography on silica gel (20% ethyl acetate in hexane), which gave the pure product as yellow powder (2.5 g, 28%). HR-MS Calcd for $C_{44}H_{70}N_2S_4$ $[M+H]^+$: 755.45001. Found: 755.45007. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 2H), 7.02 (s, 2H), 2.55 (d, *J* = 7.2 Hz, 4H), 1.70–1.60 (m, 2H), 1.40–1.20 (m, 36H), 0.86 (t, *J* = 7.0 Hz, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.9, 149.8, 143.5, 137.1, 128.6, 124.5, 39.0, 35.1, 33.4, 32.1, 32.0, 30.1, 29.8, 26.71, 26.69, 22.8,14.3.

*2,5-Bis(5-bromo-4-(2-butyloctyl)thiophen-2-yl)thiazolo[5,4-d]thiazole (**3a**).*

To a solution of **2a** (0.64 g, 1.0 mmol) in chloroform (40 mL), NBS (0.39 g, 2.2 mmol) was added, and stirred 6 hours at 50 °C. The reaction solution was cooled to rt, and washed with water, and then dried over anhydrous $MgSO_4$. After the removal of solvents, the crude product was purified by column chromatography on silica gel (20% ethyl acetate in hexane), which was followed by recrystallization from hexane:ethanol = 1:2, giving the pure product as yellow powder (0.68 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 2H), 2.51 (d, *J* = 7.2 Hz, 4H), 1.70–1.60 (m, 2H), 1.40–1.20 (m, 24H), 0.86 (t, *J* = 7.0 Hz, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.0, 149.9, 142.9, 136.6, 127.9, 114.2, 38.7, 34.4, 33.4, 33.1, 32.0, 29.8, 28.9, 26.6, 23.2, 22.8, 14.3. HRMS Calcd for $C_{36}H_{52}Br_2N_2S_4$ $[M+H]^+$: 799.14583. Found: 799.14589.

*2,5-Bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)thiazolo[5,4-d] thiazole (**3b**).*

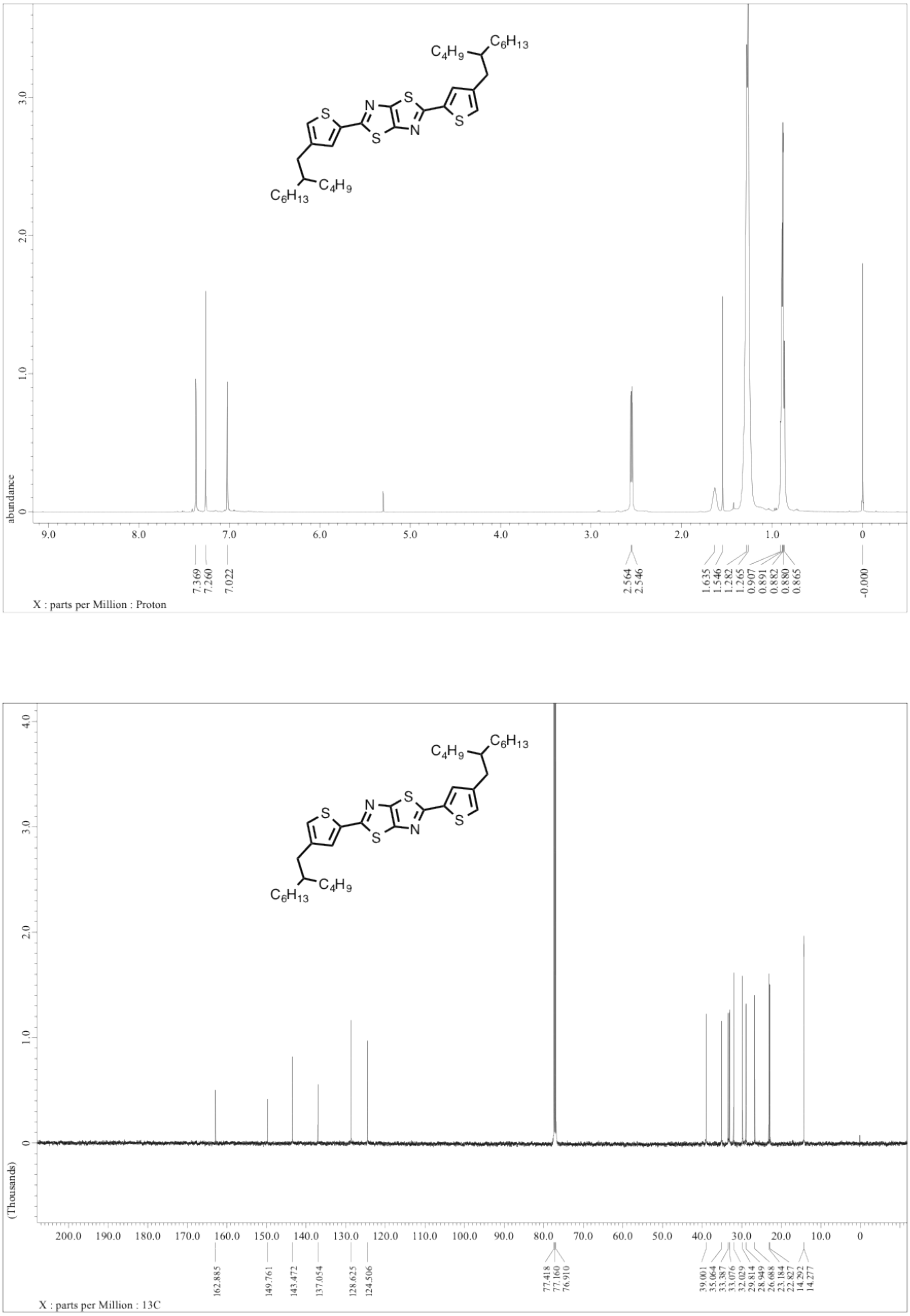
To a solution of **2a** (0.76 g, 1.0 mmol) in chloroform (40 mL), NBS (0.39 g, 2.2 mmol) was added and stirred 6 hours at 50 °C. The reaction solution was cooled to rt, and washed with water, and then dried over anhydrous $MgSO_4$. After the removal of solvents, the crude product was purified by column chromatography on silica gel (20% ethyl acetate in hexane), which was followed by recrystallization from hexane:ethanol = 1:2, giving the pure product as yellow powder (0.75 g, 82%). HRMS Calcd for $C_{44}H_{70}Br_2N_2S_4$ $[M+H]^+$: 911.27103. Found: 911.27109. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 2H), 2.51 (d, J = 7.2 Hz, 4H), 1.70–1.60 (m, 2H), 1.40–1.20 (m, 36H), 0.86 (t, J = 7.0 Hz, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.0, 149.9, 142.9, 136.6, 127.9, 114.2, 38.7, 34.4, 33.4, 33.1, 32.0, 29.8, 28.8, 26.6, 23.2,22.8,14.3.

General procedure for polymerization.

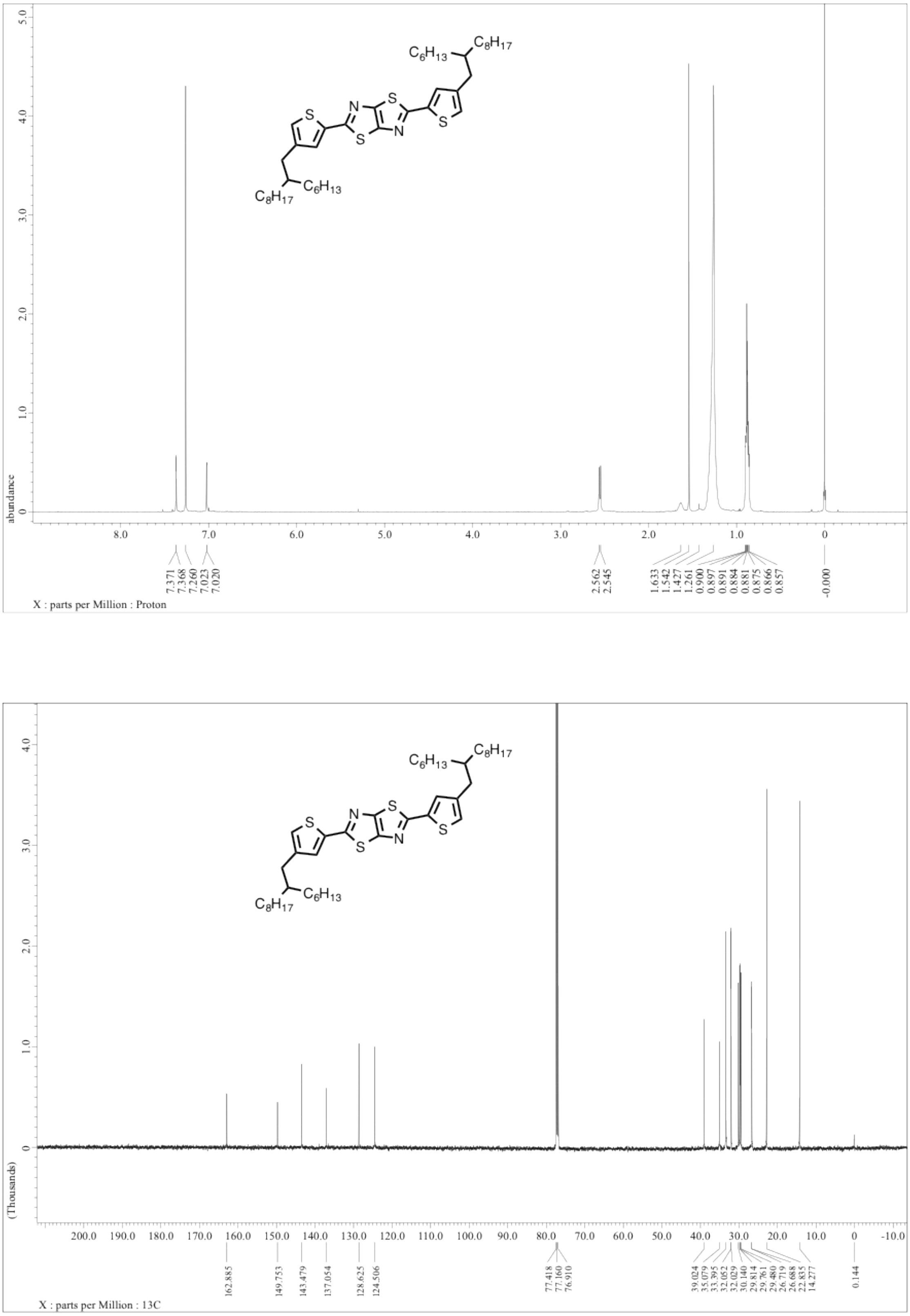
To a reaction tube equipped with a stirring bar, stannylated monomer (0.10 mmol), brominated monomer (0.10 mmol), $Pd(PPh_3)_4$ (2.3 mg, 0.002 mmol), and chlorobenzene (5 ml) were added. Then the tube was purged with argon and sealed. The reaction tube was set into a microwave reactor and heated to 180 °C for 40 min. After cooling to room temperature, the reaction solution was poured into 200 mL of methanol containing 5 mL of hydrochloric acid, and stirred for 5 hours. Then the precipitated solid was subjected to the sequential Soxhlet extraction with methanol, hexane to remove low molecular weight fractions. The residue was then extracted with chloroform and chlorobenzene, and reprecipitated in 200 mL of methanol to yield dark purple or dark blue solids (yield = 88–93%).

iPTzBT-BOBO: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 2H), 7.42 (s, 2H), 3.26 (d, J = 7.2 Hz, 4H), 3.07 (d, J = 7.2 Hz, 4H), 2.16–2.20 (m, 2H), 2.10–2.16 (m, 2H), 1.40–1.70 (m, 48H), 1.0–1.2 (m, 24H).

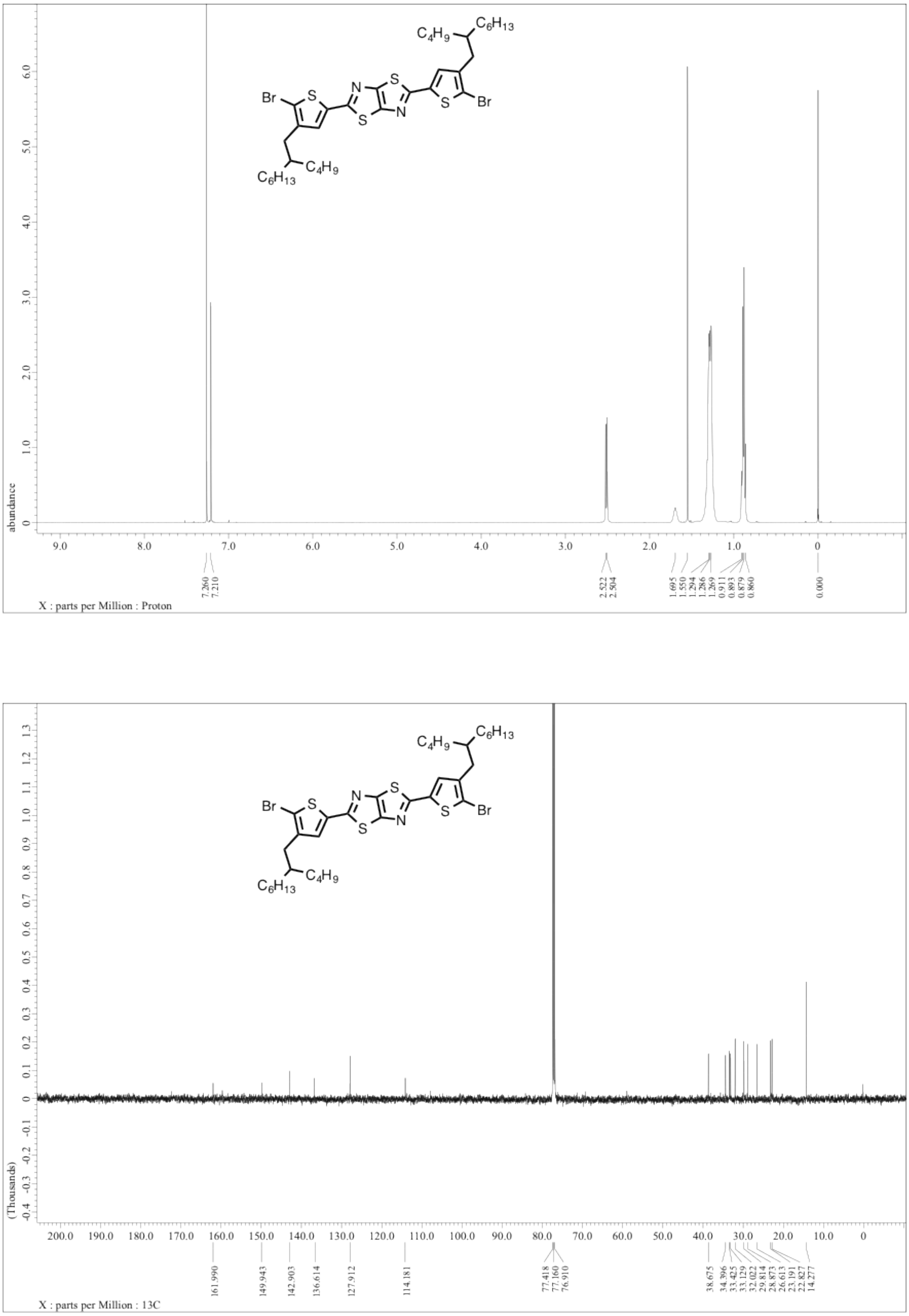
iPTzBT-BOHD: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 2H), 7.43 (s, 2H), 3.28 (d, J = 7.2 Hz, 4H), 3.09 (d, J = 7.2 Hz, 4H), 2.16–2.20 (m, 2H), 2.08–2.15 (m, 2H), 1.40–1.70 (m, 60H), 1.0–1.2 (m, 24H).



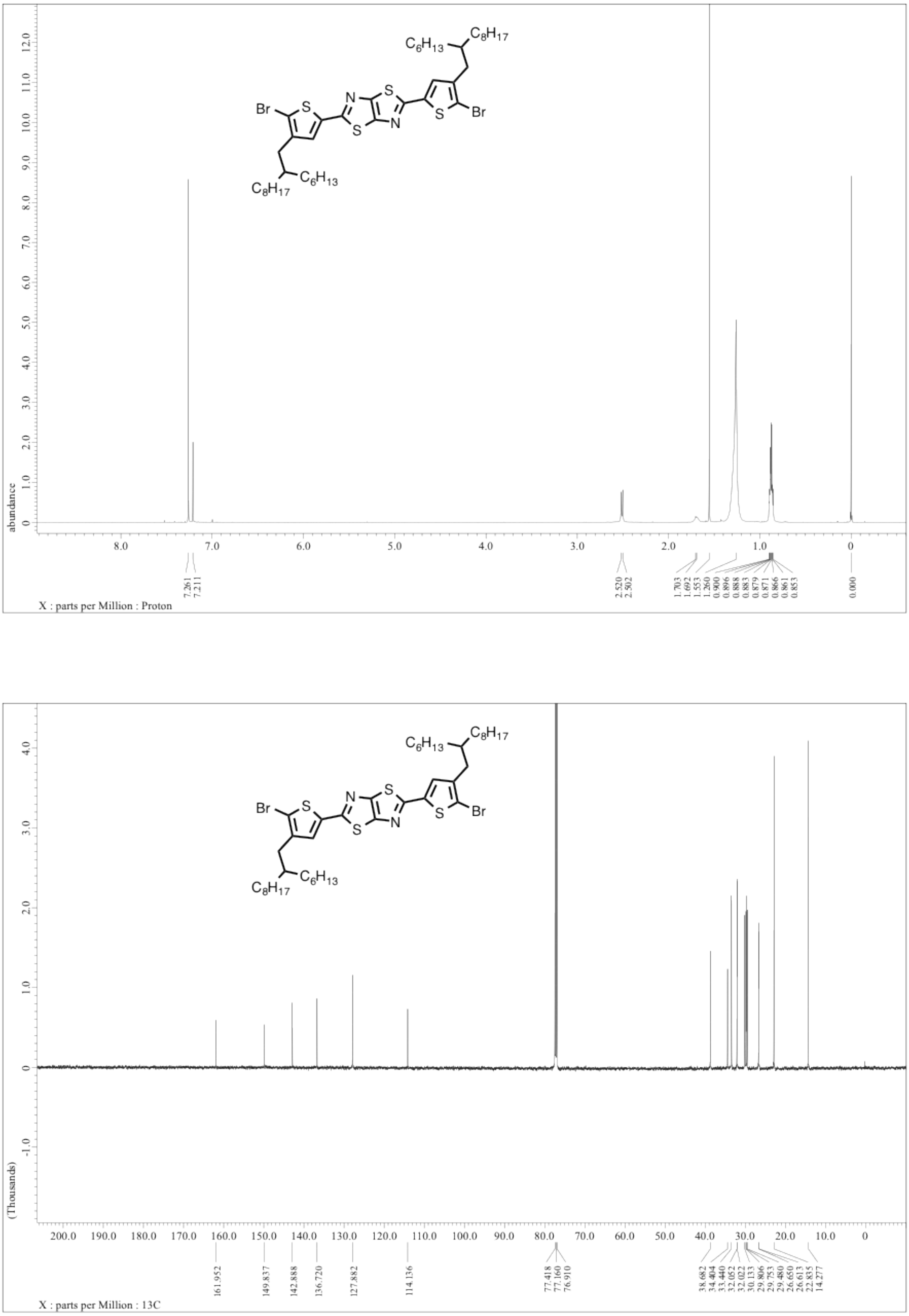
^{1}H- (upper) and ^{13}C-NMR (lower) spectra of **2a**.



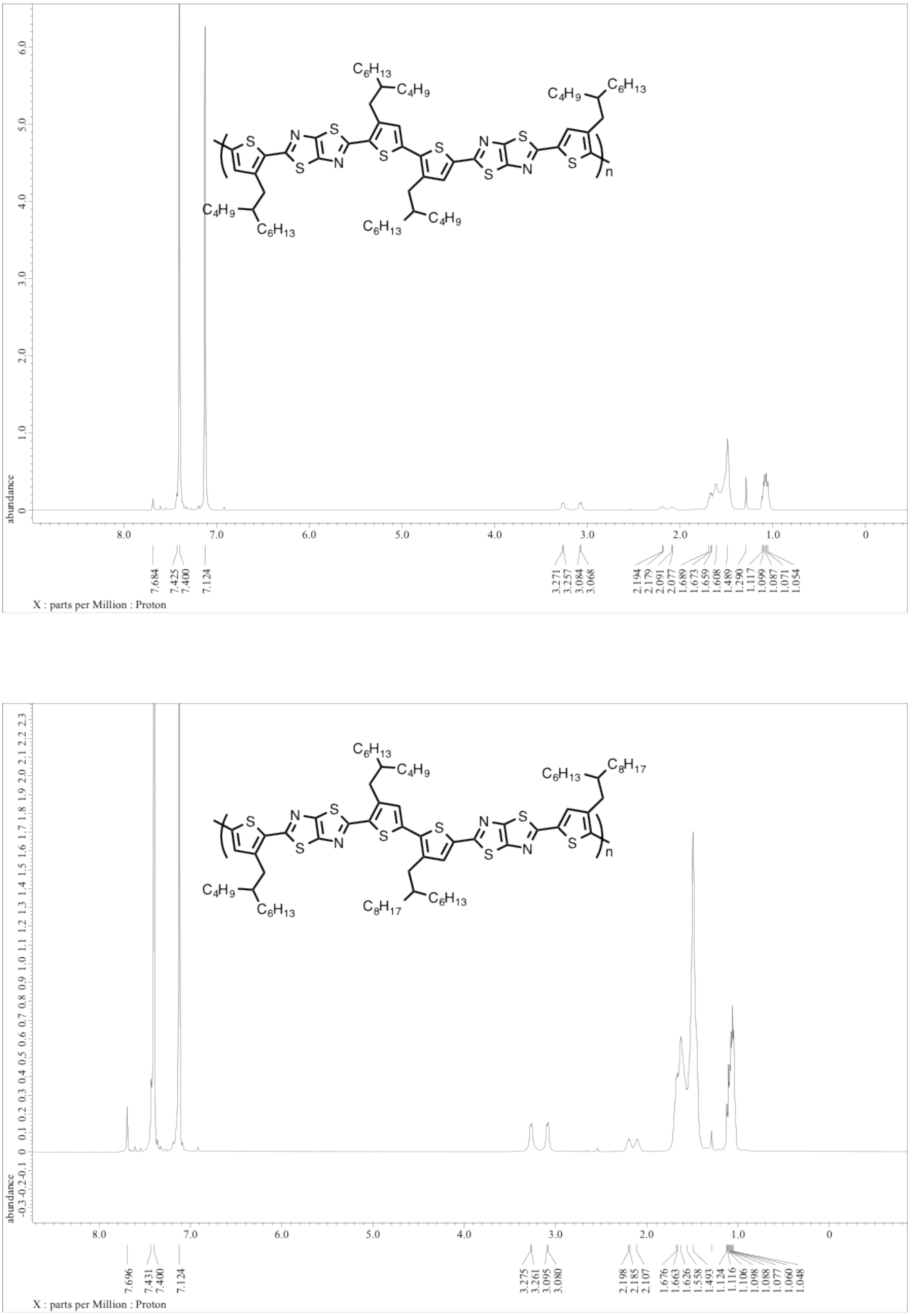
^{1}H- (upper) and ^{13}C-NMR (lower) spectra of **2b**.



^{1}H- (upper) and ^{13}C-NMR (lower) spectra of **3a**.



^{1}H- (upper) and ^{13}C-NMR (lower) spectra of **3b**.



^{1}H-NMR spectra of iPTzBT-BOBO (upper) and iPTzBT-BOHD (lower).

Instrumentation.

UV-vis absorption spectra were measured using a Shimadzu UV-3600 spectrometer. Photoemission yield spectra were measured by using a photoelectron spectrometer, model AC-2, in air (Riken Keiki Co., Ltd). Dynamic force-mode atomic force microscopy study was carried out on a Nanocute scanning probe microsope system (SII Nanotechnology, Inc.). Differential scanning calorimetry (DSC) was performed with EXSTAR DSC7020 (SII Nanotechnology, Inc.) at 10 °C/min for both heating and cooling processes.

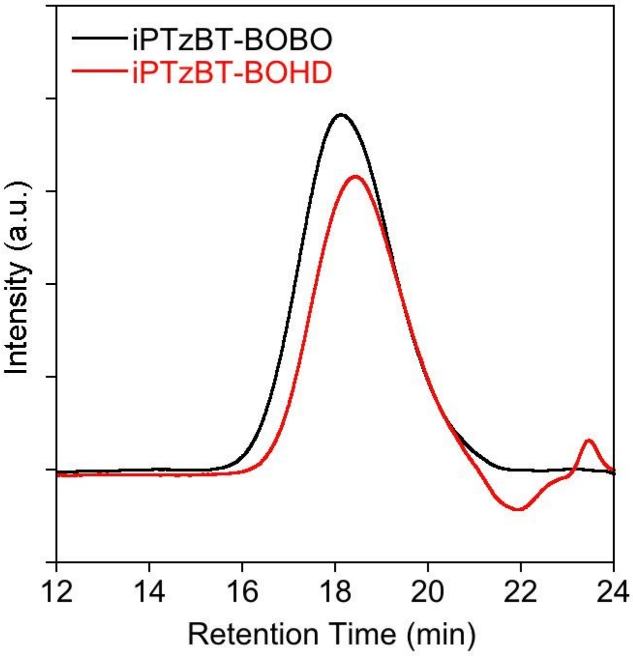


Figure S1. GPC chromatograms of iPTzBT-BOBO and iPTzBT-BOHD

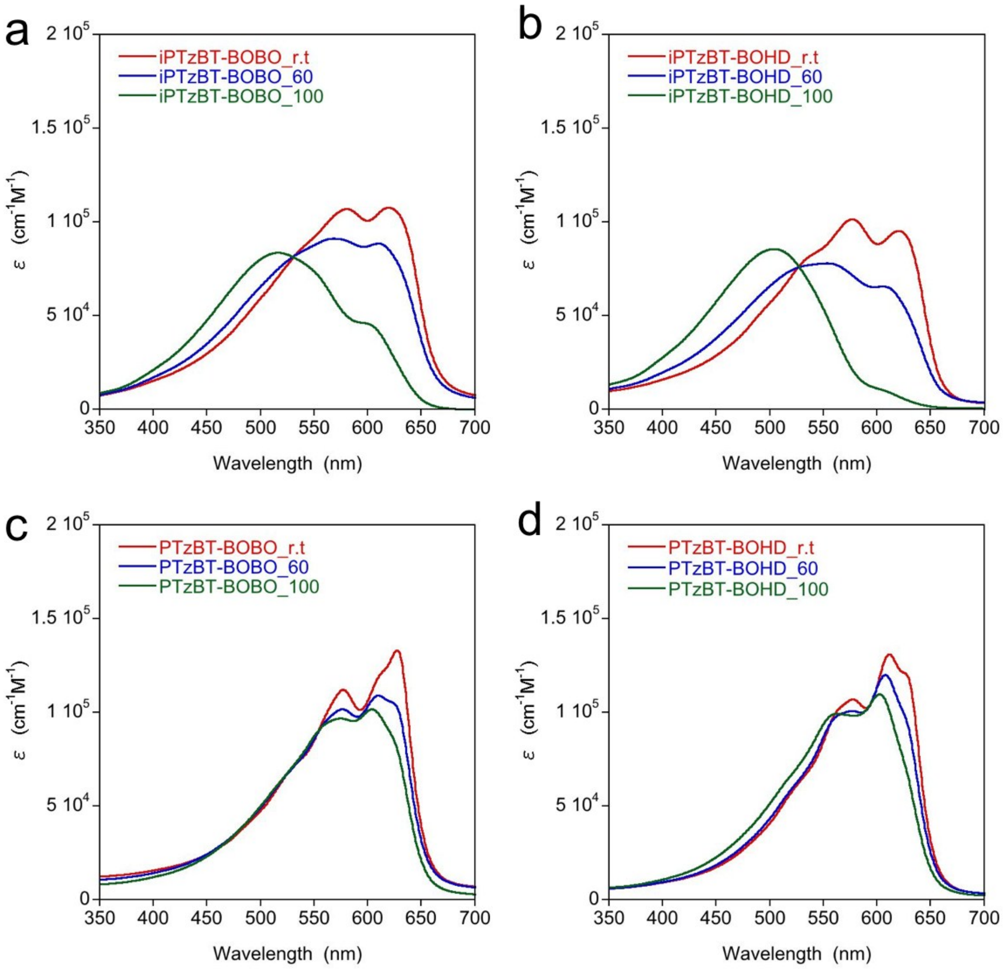


Figure S2. Temperature dependent UV-vis absorption spectra of PTzBTs (a, b) and iPTzBTs (c, d) in chlorobenzene solution.

Table S1. Absorption maxima (λ_{max}) of iPTzBTs and PTzBTs obserbved in the temperature-dependent UV-vis absorption measurement.

Polymer	λ_{max} [nm]		
	r.t	60 °C	100 °C
iPTzBT-BOBO	581, 620	568, 610	517
iPTzBT-BOHD	577, 620	553, 606	504
PTzBT-BOBO	577, 628	576, 610	575, 604
PTzBT-BOHD	578, 612	577, 608	563, 603

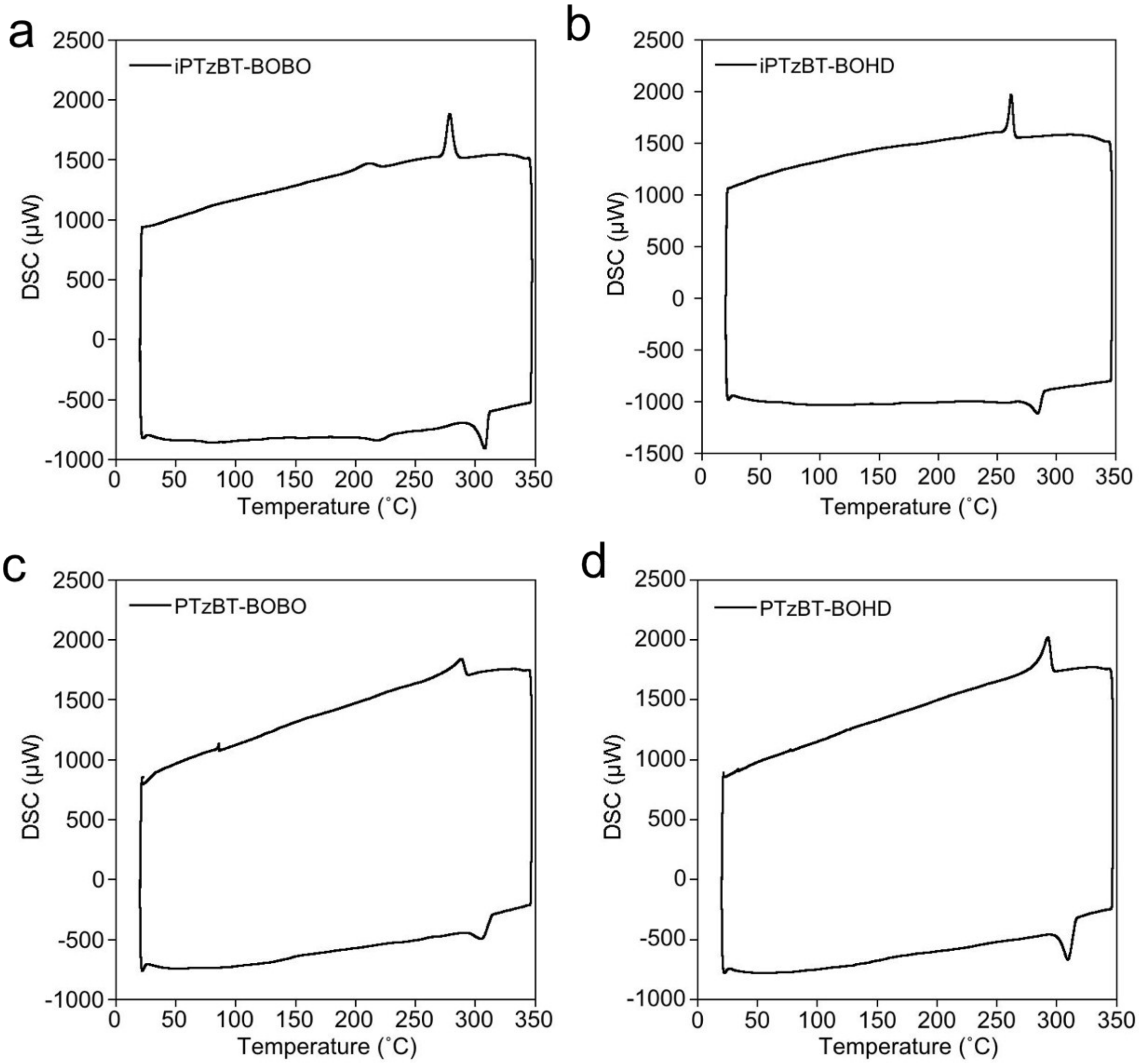


Figure S3. DSC curve of the iPTzBT-BOBO, iPTzBT-BOHD, PTzBT-BOBO and PTzBT-BOHD.

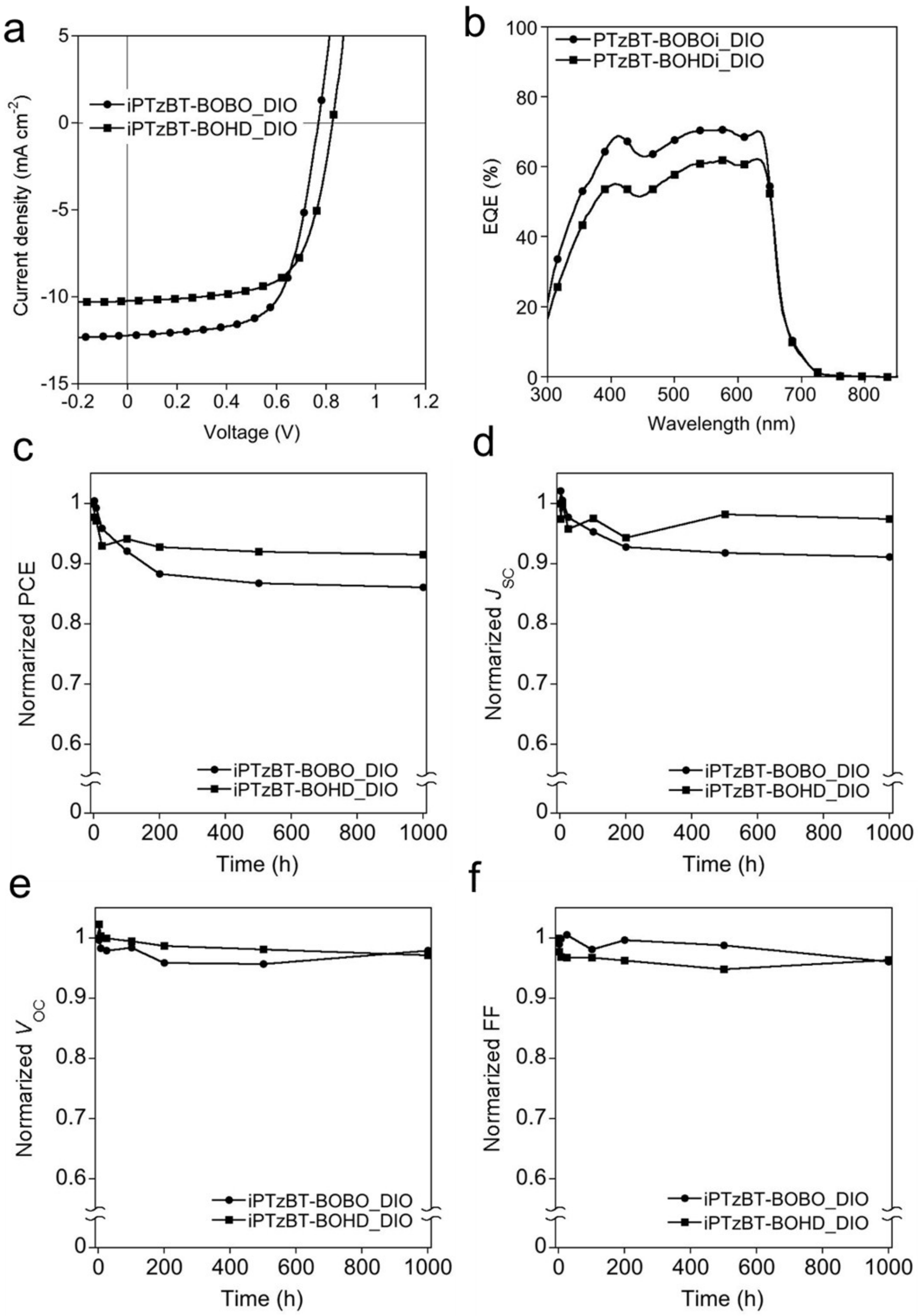


Figure S4. (a, b) Photovoltaic characteristics of the solar cells based on iPTzBTs fabricated from CB solution including 1% of DIO as the solvent additive. (c-f) Relative change of the photovoltaic parameters by annealing the cells at 85 °C in the dark in the glovebox for 1000 hours. (c) PCE, (d) J_{SC}, (e) V_{OC}, and (f) FF.

Table S2. Photovoltaic properties of the solar cells based on iPTzBTs fabricated from CB solution including 1% of DIO as the solvent additive.

	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	PCE (%)[a]
iPTzBT-BOBO	12.2	0.77	0.65	6.1 (5.8)
iPTzBT-BOHD	10.2	0.82	0.64	5.3 (5.1)

[a] Maximum values and average values in the brackets.

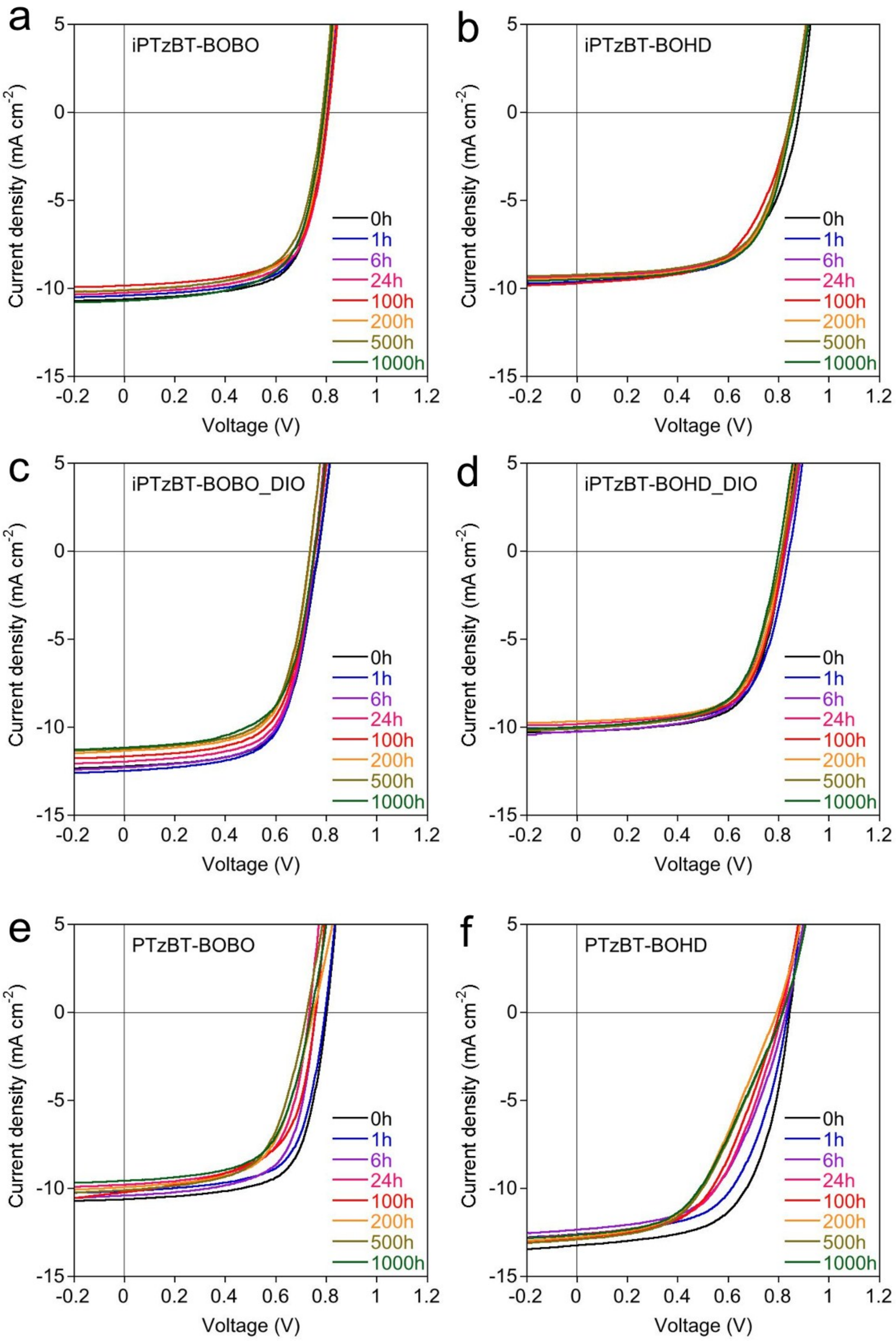


Figure S5. *J–V* curves of the solar cells based on iPTzBT-BOBO (a), iPTzBT-BOHD (b), iPTzBT-BOBO with 1 vol% of DIO (c), iPTzBT-BOHD with 1 vol% of DIO (d), PTzBT-BOBO (e), and iPTzBT-BOHD (f).

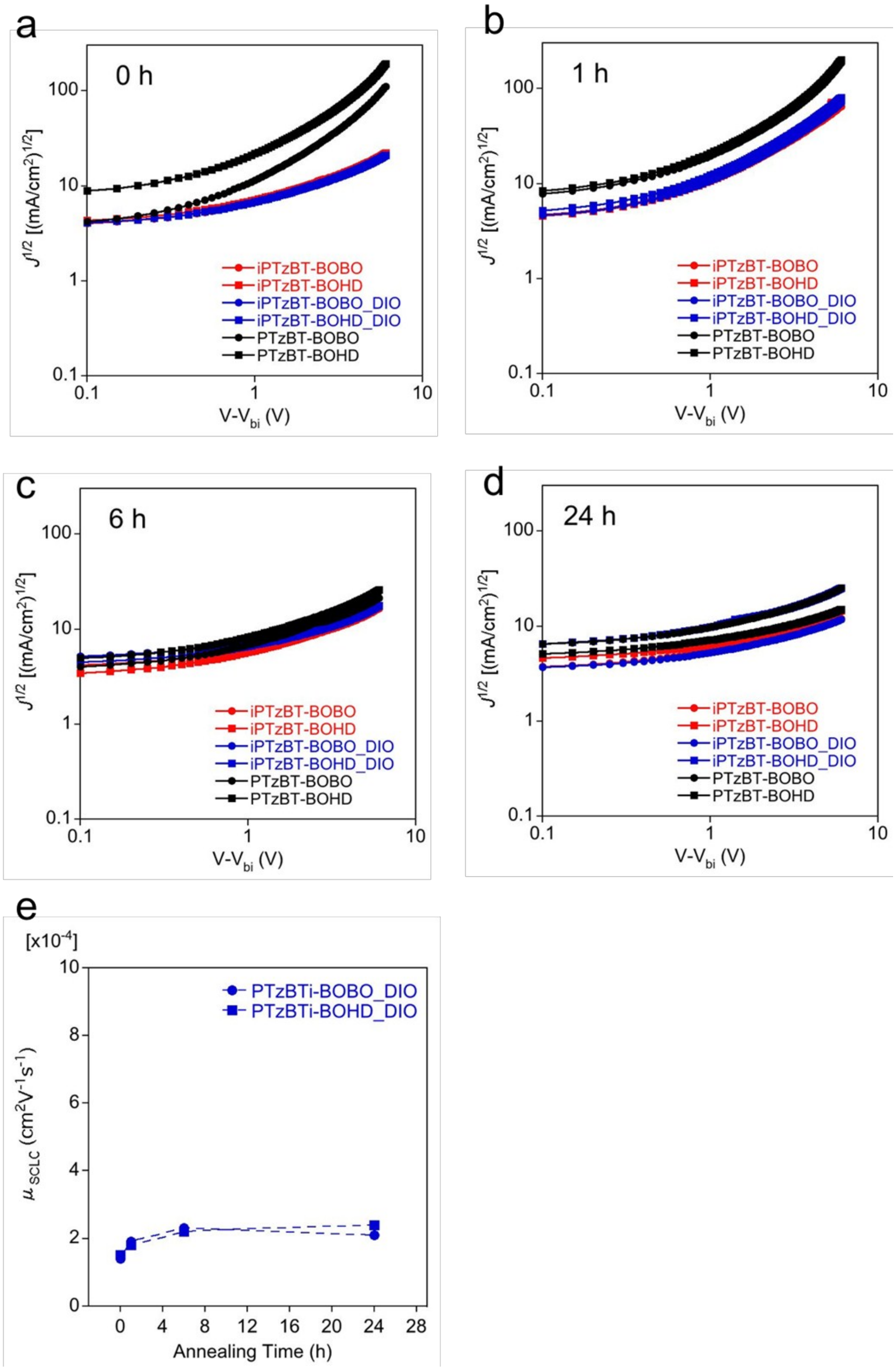


Figure S6. (a–d) *J*–*V* curves of the hole-only devices for as spun films (a), and the films annealed at 85 °C for 1 hour (b), 6 hours (c), and 24 hours (d). Change of charge carrier mobilities (μ_{SCLC}) estimated from the space-charge-limited-current model using iPTzBTs and PTzBTs fabricated by CB with 1 vol% DIO (e) under the storage for 24 hours at 85 °C in the glovebox.

Table S3. Charge carrier mobilities (μ_{SCLC}).

Polymer	μ_{SCLC} (cm^{2}V^{-1}s-^{1})			
	0 h	1 h	6 h	24 h
iPTzBT-BOBO	1.8×10^{-4}	2.3×10^{-4}	2.1×10^{-4}	2.1×10^{-4}
iPTzBT-BOHD	1.7×10^{-4}	2.1×10^{-4}	1.9×10^{-4}	2.0×10^{-4}
iPTzBT-BOBO_DIO	1.4×10^{-4}	1.9×10^{-4}	2.3×10^{-4}	2.1×10^{-4}
iPTzBT-BOHD_DIO	1.5×10^{-4}	1.8×10^{-4}	2.2×10^{-4}	2.4×10^{-4}
PTzBT-BOBO	5.5×10^{-4}	6.1×10^{-4}	2.7×10^{-4}	2.3×10^{-4}
PTzBT-BOHD	6.1×10^{-4}	6.2×10^{-4}	2.5×10^{-4}	2.1×10^{-4}

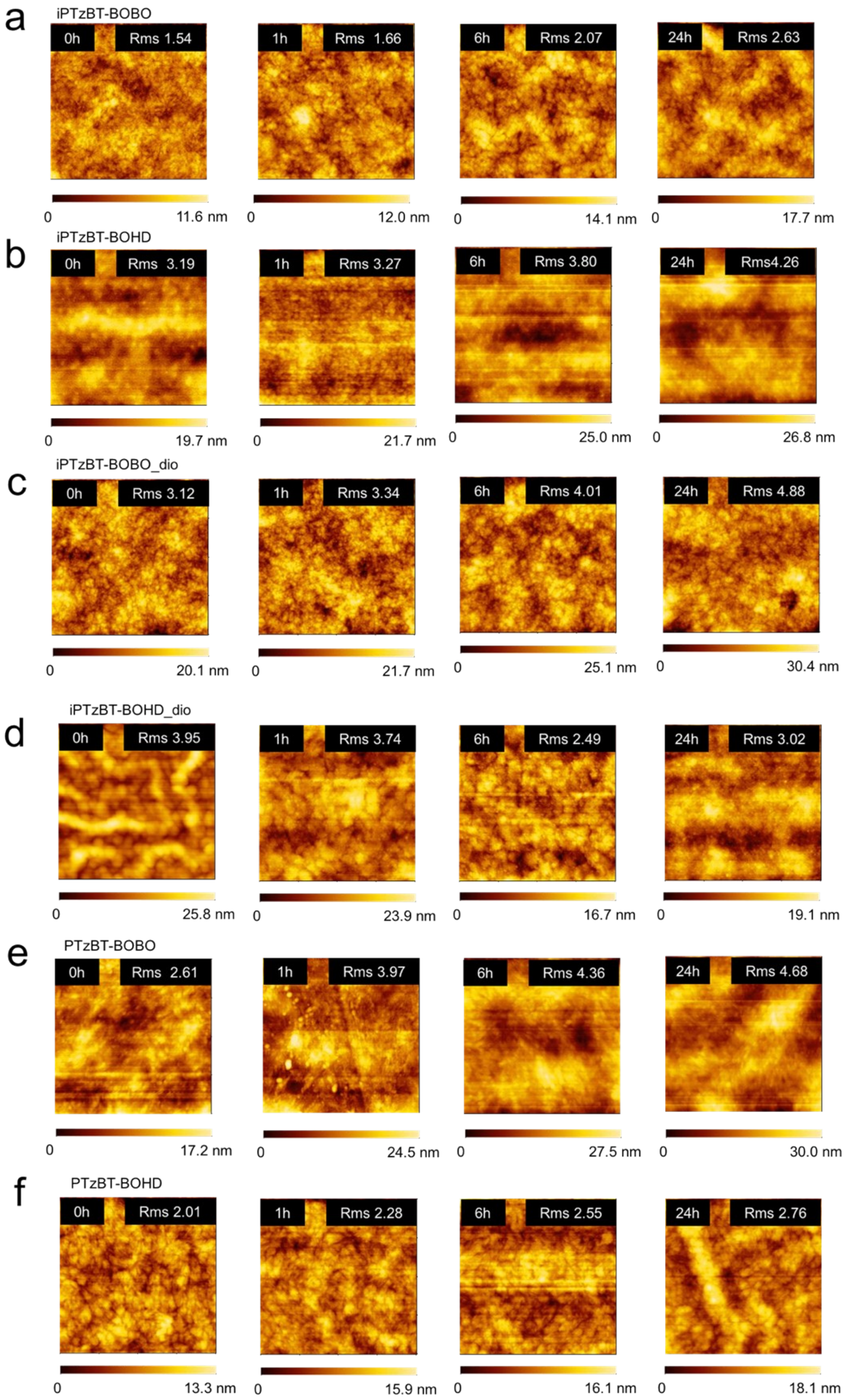


Figure S7. AFM images of the blend films for iPTzBT-BOBO/$PC_{71}BM$ (a), iPTzBT-BOHD/$PC_{71}BM$ (b), iPTzBT-BOBO/$PC_{71}BM$ with DIO (c), iPTzBT-BOHD/$PC_{71}BM$ with DIO (d), PTzBT-BOBO/$PC_{71}BM$ (e), and PTzBT-BOBO/$PC_{71}BM$ (f).

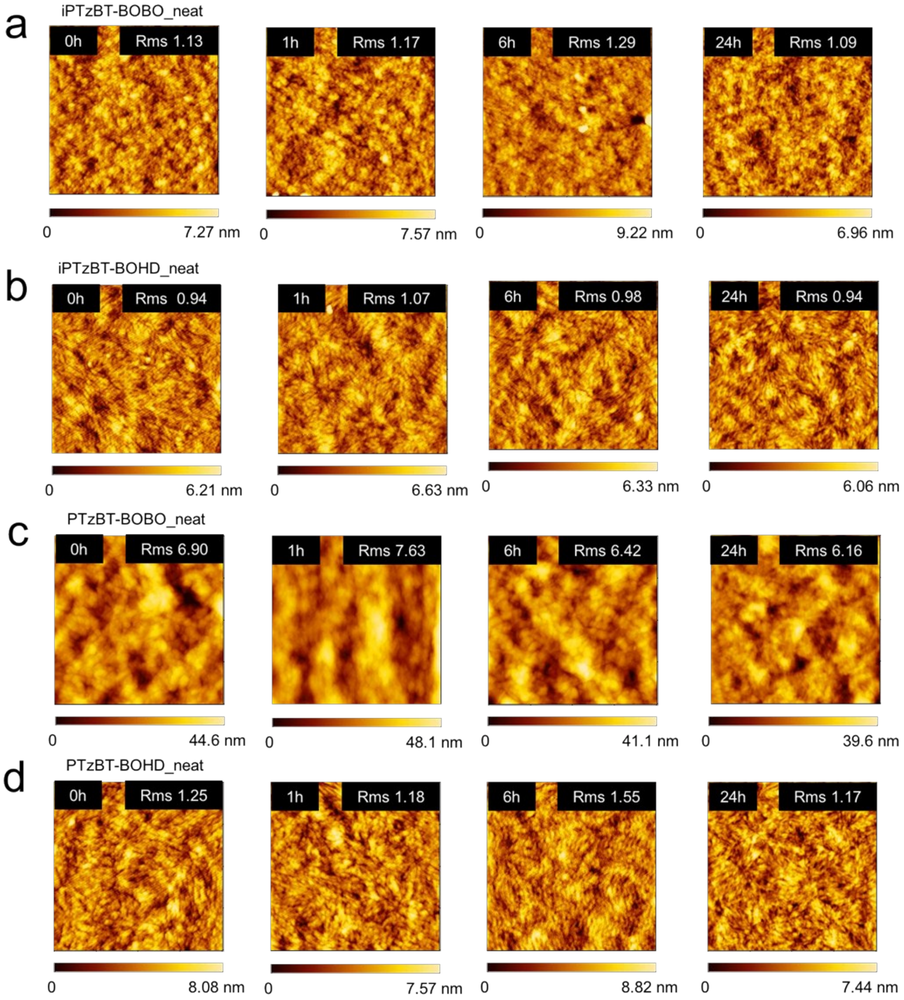


Figure S8. AFM images of iPTzBT-BOBO (a), iPTzBT-BOHD (b), PTzBT-BOBO (c), and PTzBT-BOHD (d) neat films before and after annealing at 85 °C for 1, 6, and 24 hours.

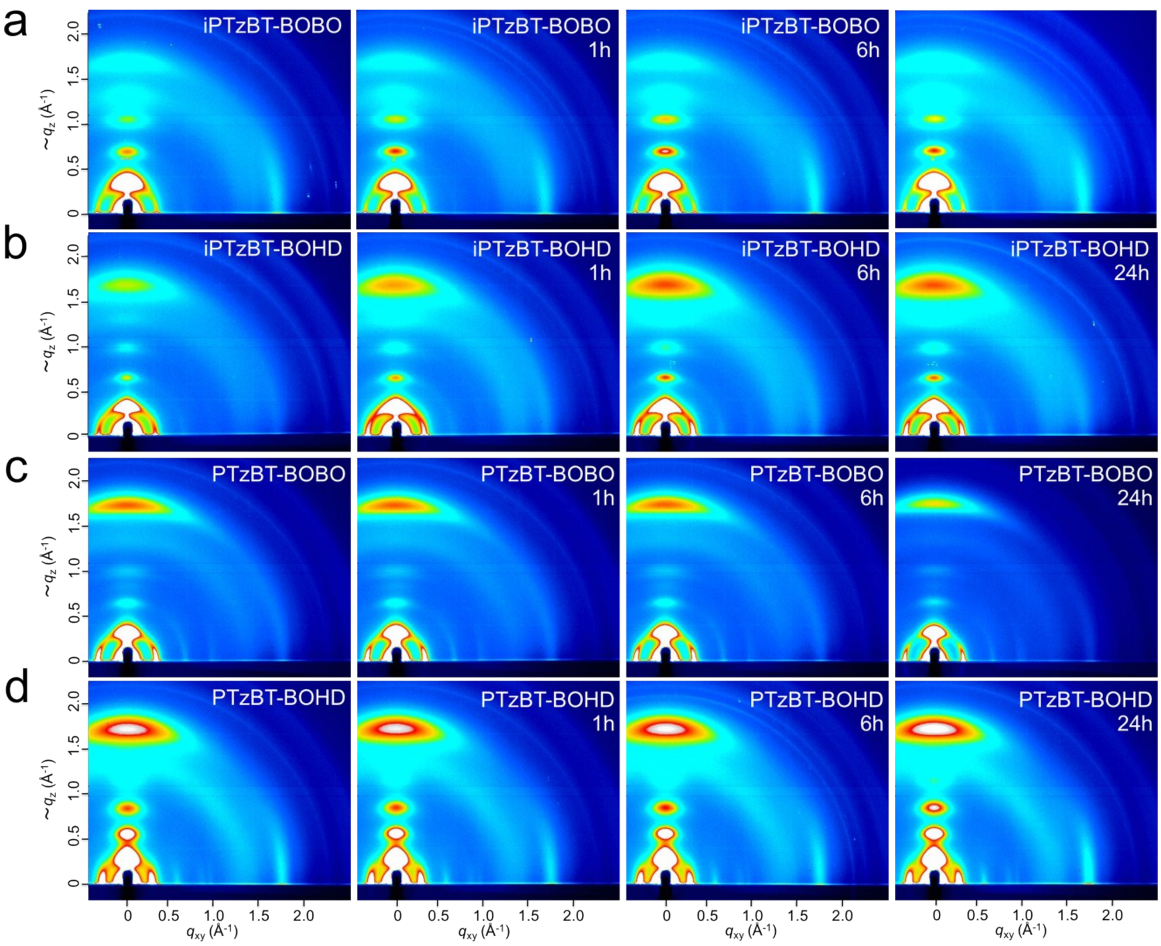


Figure S9. 2D GIXD patterns of iPTzBT-BOBO (a), iPTzBT-BOHD (b), PTzBT-BOBO (c), and PTzBT-BOHD (d) neat films before and after annealing at 85 °C for 1, 6, and 24 hours.

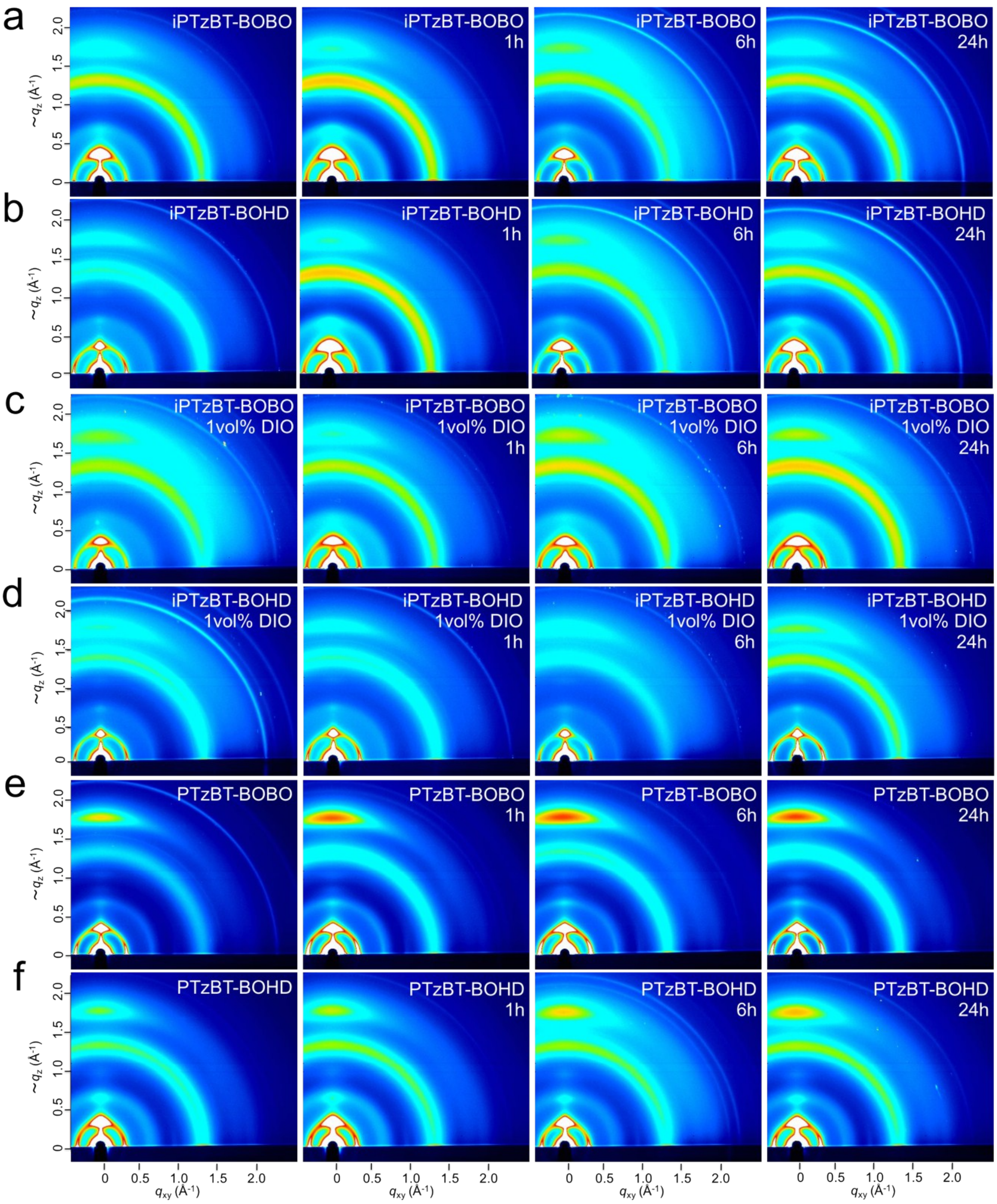


Figure S10. 2D GIXD patterns of the iPTzBT-BOBO/PC$_{71}$BM film (a), iPTzBT-BOBO/PC$_{71}$BM film (b), DIO-aided iPTzBT-BOBO/PC$_{71}$BM film (c), DIO-aided iPTzBT-BOHD/PC$_{71}$BM film (d), PTzBT-BOBO/PC$_{71}$BM film (e), and PTzBT-BOHD/PC$_{71}$BM film (f), before and after annealing at 85 °C for 1, 6, and 24 hours.

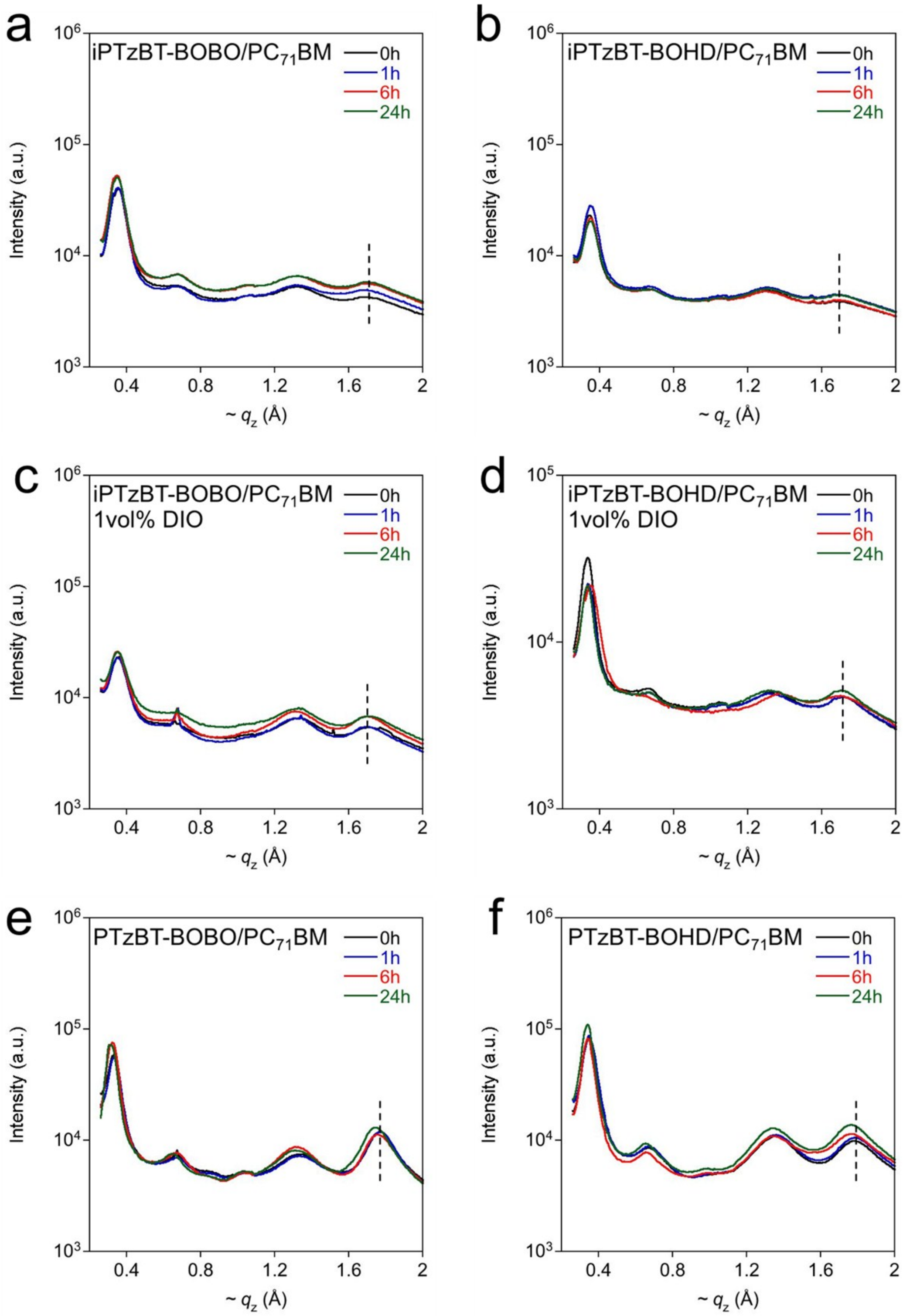


Figure S11. Cross-sectional profiles, cut from the 2D GIXD patterns along the ~q_z axis, of the polymer/PC$_{71}$BM blend films (as-spun and annealed for 1, 6, and 24 hours at 85 °C) for iPTzBT-BOBO/PC$_{71}$BM (a), iPTzBT-BOHD/PC$_{71}$BM film (b), iPTzBT-BOBO/PC$_{71}$BM with DIO (c), iPTzBT-BOHD/PC$_{71}$BM with DIO (d), PTzBT-BOBO/PC$_{71}$BM (e), and PTzBT-BOHD/PC$_{71}$BM (f).

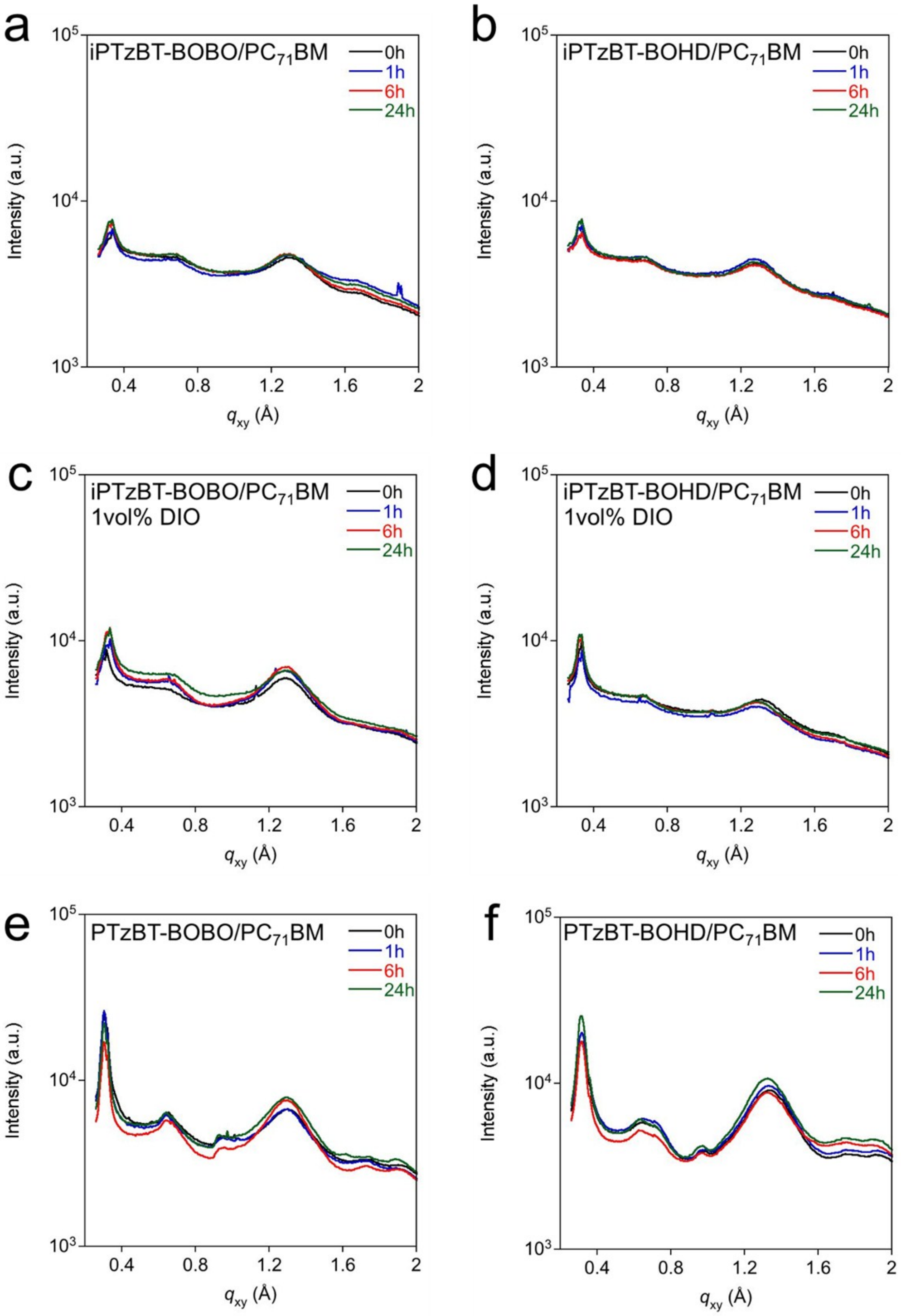


Figure S12. Cross-sectional profiles, cut from the 2D GIXD patterns along the ~q_{xy} axis, of the polymer/PC$_{71}$BM blend films (as-spun and annealed for 1, 6, and 24 hours at 85 °C) for iPTzBT-BOBO/PC$_{71}$BM (a), iPTzBT-BOHD/PC$_{71}$BM film (b), iPTzBT-BOBO/PC$_{71}$BM with DIO (c), iPTzBT-BOHD/PC$_{71}$BM with DIO (d), PTzBT-BOBO/PC$_{71}$BM (e), and PTzBT-BOHD/PC$_{71}$BM (f).

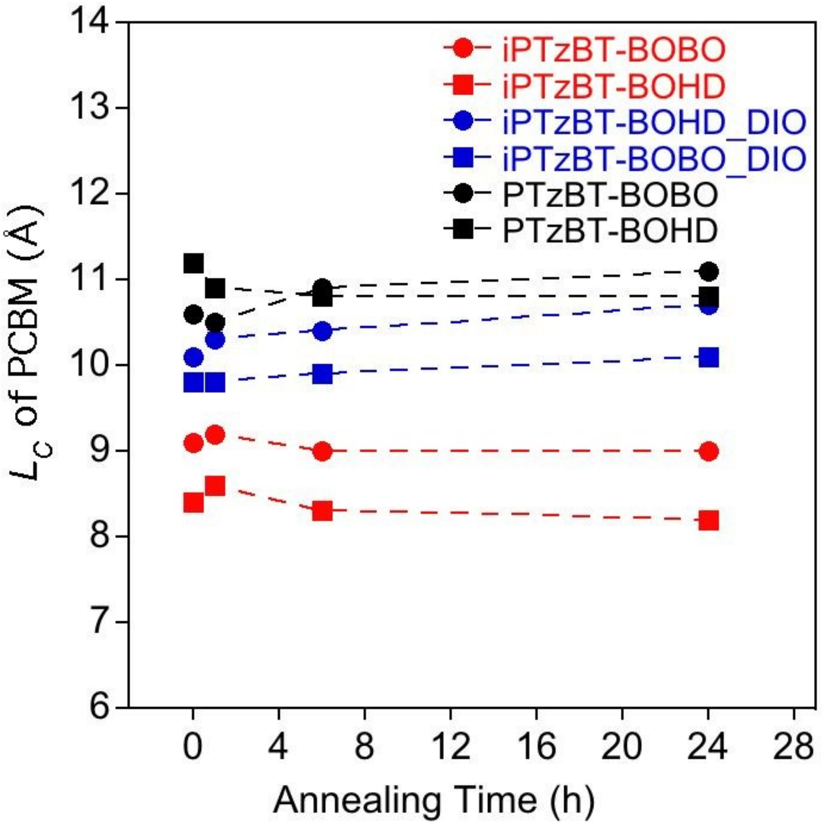


Figure S13. Change of the coherence length (L_C) of $PC_{71}BM$ in the blend films estimated from the modified Scherrer's equation ($L_C = 2\pi/\mathrm{FWHM}$).

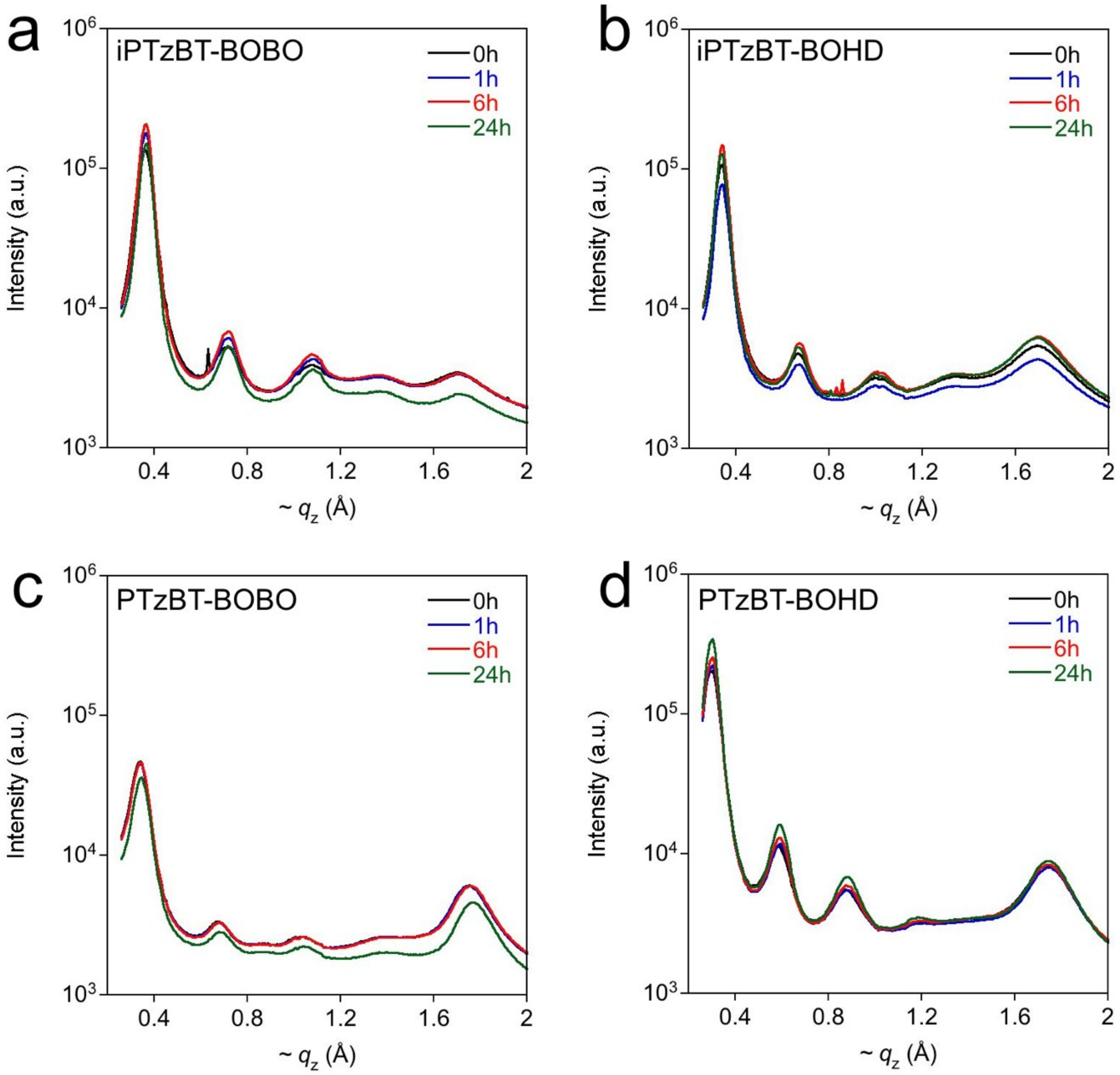


Figure S14. Cross-sectional profiles, cut from the 2D GIXD patterns along the ~q_z axis, of the polymer neat films (as-spun and annealed for 1, 6, and 24 hours at 85 °C) for iPTzBT-BOBO film (a), iPTzBT-BOHD film (b), PTzBT-BOBO film (c), PTzBT-BOHD film (d).

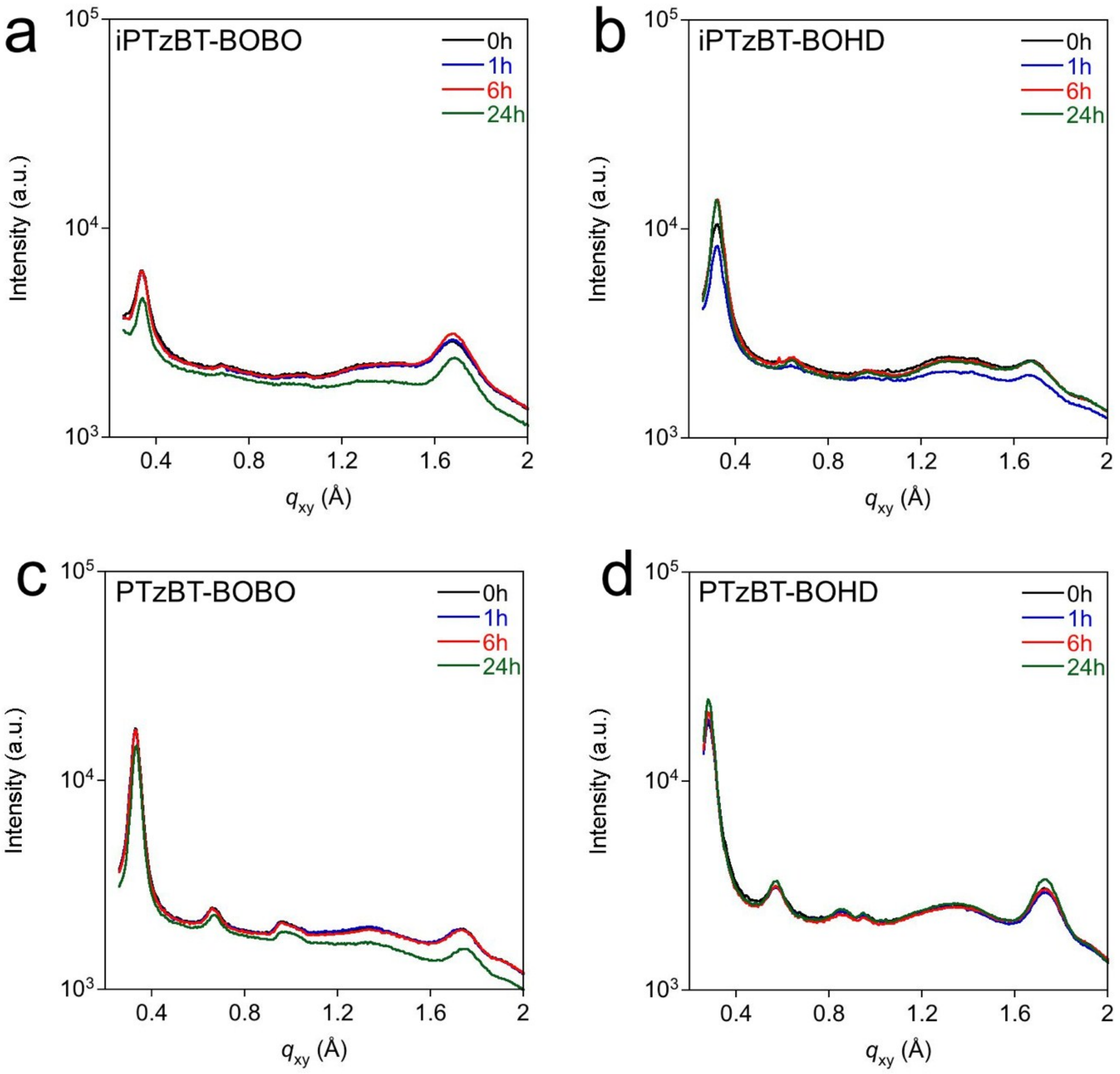


Figure S15. Cross-sectional profiles, cut from the 2D GIXD patterns along the ~q_{xy} axis, of the polymer neat films (as-spun and annealed for 1, 6, and 24 hours at 85 °C) for iPTzBT-BOBO film (a), iPTzBT-BOHD film (b), PTzBT-BOBO film (c), PTzBT-BOHD film (d).

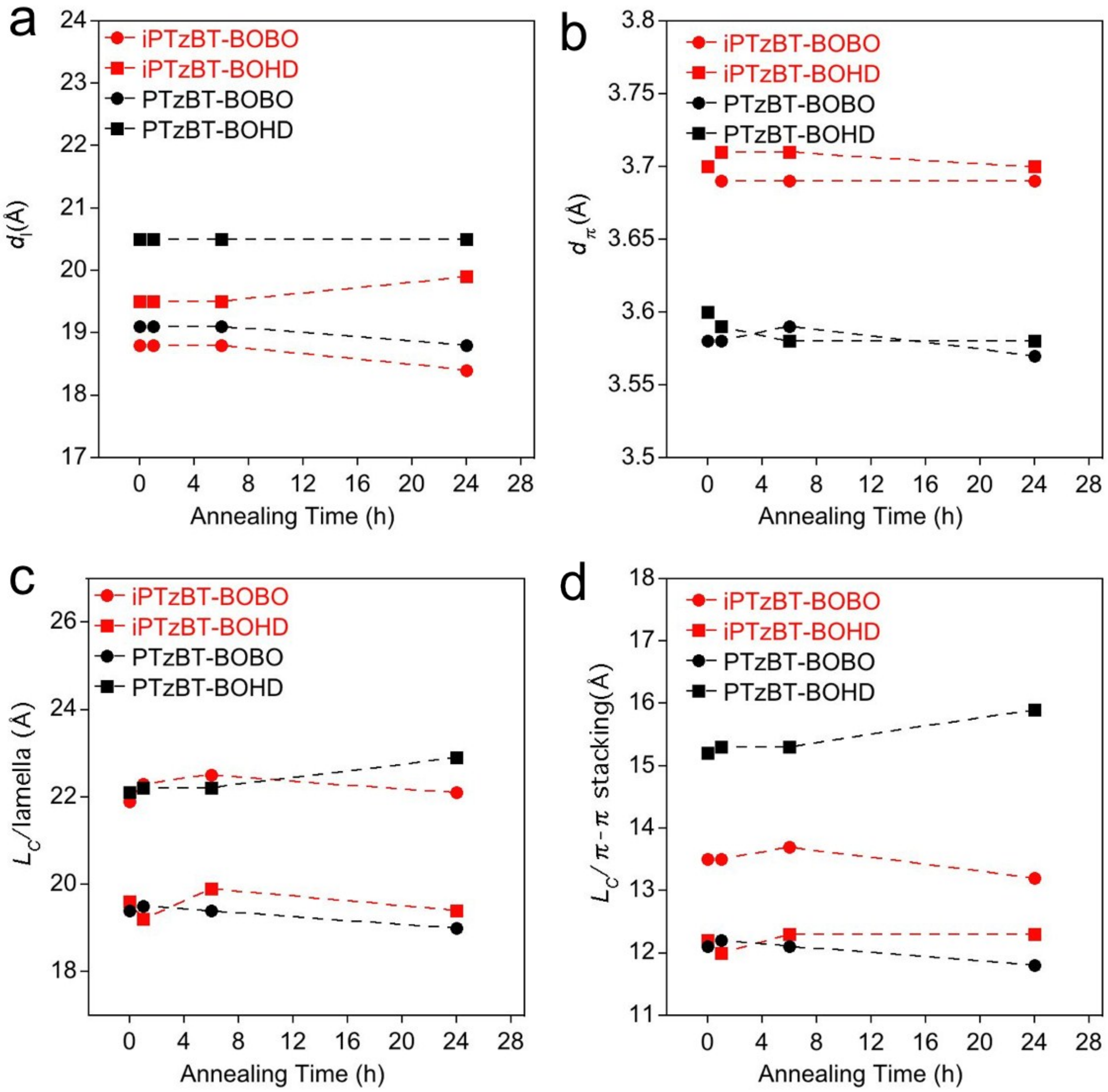


Figure S16. (a, b) Change of the intermolecular distances of the polymer neat films as a function of annealing time. (a) Lamellar distance (d_l), (b) π–π stacking distance (d_π). d_l and d_π were extracted from the cross-sectional profiles of the 2D GIXD patterns along the q_z and q_{xy} axis, respectively. (c, d) Change of the coherence length (L_C) estimated from the Scherrer's equation (L_C =2π/FWHM) using the diffraction peaks of the face on crystallites. (c) Lamellar structure, (d) π–π stacking structure.

Reference.

S1 S. Wen, Q. Dong, W. Chemg, P. Li, B. Xu, W. Tian, *Sol. Energy Mater. Sol. Cells.* 2012, ***100***, 239–245.

S2 I. Osaka, M. Saito, T. Koganezawa, K. Takimiya, *Adv. Mater.* 2014, ***26***, 331–338.