

Supporting Information for

A Case Study on Thermal-stability of Polymerized Small Molecular Acceptor based Polymer Solar Cells

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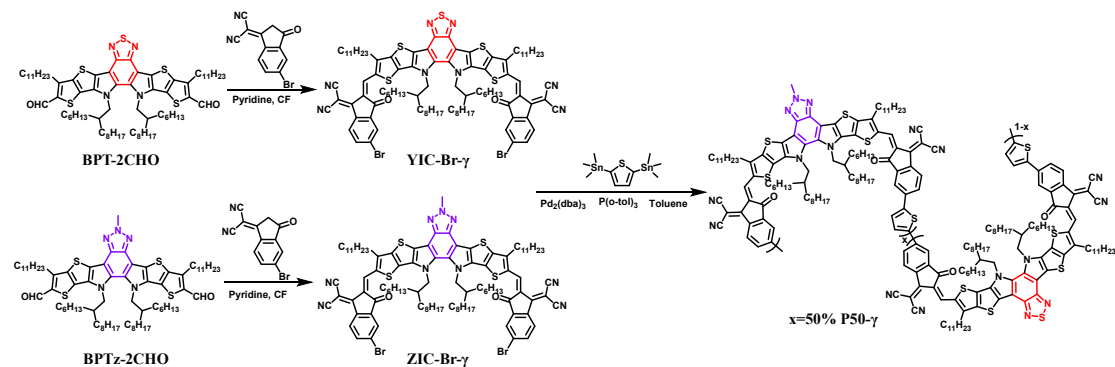
1. General characterization

Nuclear magnetic resonance (NMR) spectra of the compounds were collected using Bruker AVANCE 400 or 600 MHz spectrometers with deuterated chloroform (CDCl_3) as the solvent and tetramethylsilane (TMS) as the internal reference. Decomposition temperature (with 5% weight loss) was determined by thermal gravimetric analysis (TGA) (NETZSCH STA 449C) with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under N_2 . The photophysical and electrochemical properties were characterized by UV–visible–near-infrared spectroscopy (Shimadzu2600i spectrophotometer). Cyclic voltammetry (CV) measurements were taken on a CHI660D electrochemical workstation. The CV experiments were carried out at room temperature with a conventional three-electrode system using a glassy carbon electrode as the working electrode, Pt wire as the counter electrode, and a saturated calomel electrode as the reference electrode. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6 , 0.1 M) in acetonitrile solution was used as the supporting electrolyte, and the scan rate was 100 mV/s. Ferrocene/Ferrocenium (Fc/Fc^+) was used as the internal standard, and their energy levels are assumed at -4.8 eV relative to the vacuum. Small molecules were dropped and cast onto the glassy carbon electrode from chloroform solutions (1 mg/mL) to form thin films. Differential scanning calorimetry (DSC) measurements were performed with a heating/cooling rate of $10\text{ }^\circ\text{C min}^{-1}$ under N_2 . The surface morphology of the films was characterized using AFM (Advanced Scanning Probe Microscope, XE-100, PSIA) in tapping mode. 2D GIWAXS measurements were performed at beamline 7.3.34 at the Advanced Light Source. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12° - 0.16° , selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector.

2. Synthesis

2-(5-bromo-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC-Br- γ) was purchased from SunaTech Inc., and 2,5-bis(trimethylstannanyl)thiophene was purchased from Derthon Optoelectronic Materials Science Technology Co. LTD. PBDB-T was purchased from Solarmer Inc. and other chemicals and solvents were

purchased from Sigma, Aladdin or Energy Chemical and used without further purification. Compounds of BT-2CHO and BTz-2CHO were synthesized according to previous reports.^{1,2}



Scheme S1. The Synthesis routes for P50- γ .

Synthesis of compound YIC-Br- γ . A mixture of compound BP-2CHO (600 mg, 0.479 mmol) and IC-Br- γ (458 mg, 3.5 equiv.) in CHCl_3 (30 mL) was degassed before adding pyridine (1.0 mL) dropwise. Under the protection of N_2 , the reaction was stirred overnight at 65 °C. After removal of the solvent, the crude product was purified by a silica gel using a mixture of dichloromethane and hexane (3:7, v/v) as an eluent to afford the product (YIC-Br- γ) as a dark blue solid (684 mg, 81% yield).

^1H NMR (400 MHz, CDCl_3) δ 9.20 (s, 2H), 8.60-8.58 (d, $J = 8$ Hz, 2H), 8.04 (s, 2H), 7.89-7.87 (d, $J = 8$ Hz, 2H), 4.77-4.75 (d, $J = 8$ Hz, 4H), 3.26-3.22 (m, 4H), 2.10 (s, 2H), 1.93-1.85 (m, 4H), 1.39-0.81 (br, 132H).

Synthesis of compound ZIC-Br- γ . A mixture of compound BPTz-2CHO (650 mg, 0.520 mmol) and IC-Br- γ (497 mg, 3.5 equiv.) in CHCl_3 (30 mL) was degassed before adding pyridine (1.0 mL) dropwise. Under the protection of N_2 , the reaction was stirred overnight at 65 °C. After removal of the solvent, the crude product was purified by a silica gel using a mixture of dichloromethane and hexane (3:7, v/v) as an eluent to afford the product (ZIC-Br- γ) as a dark blue solid (778 mg, 85% yield).

^1H NMR (400 MHz, CDCl_3) δ 9.19 (s, 2H), 8.59-8.57 (d, $J = 8$ Hz, 2H), 8.03 (s, 2H), 7.87-7.85 (d, $J = 8$ Hz, 2H), 4.75-4.73 (d, $J = 8$ Hz, 4H), 4.62 (s, 3H), 3.25-3.21 (m, 4H), 2.10 (s, 2H), 2.04 (s, 2H), 1.90-1.86 (m, 4H), 1.38-0.6 (br, 99H).

Synthesis of compound P50- γ . Compound YIC-Br- γ (59.9 mg, 0.034 mmol), ZIC-

Br- γ (60.0 mg, 0.034 mmol), 2,5-bis(trimethylstannyl)thiophene (28.0 mg, 0.068 mmol), Pd₂(dba)₃ (1.25 mg, 0.0014 mmol) P(o-tol)₃ (1.66 mg, 0.0054 mmol) were combined in a 25 mL sealed tube. Dry toluene (Tol.) (8 mL) was added under the N₂ atmosphere. The mixture was stirred at 115°C for 72 h. After cooling down to room temperature, the reactant mixture was poured into MeOH (30 mL). The precipitate was filtered and the obtained solid was chromatographically purified on a silica gel column eluted with chloroform. Then the collected product was dissolved by 2 mL of chloroform and precipitated into methanol. The solid was filtered and dried under vacuum to give the dark solid **P50- γ** (82 mg, 63% yield), GPC: M_n = 8.6 kDa, M_w = 14.9 kDa; PDI = 1.72.

¹H NMR (600 MHz, CDCl₃) δ 9.28-9.23 (br, 4H), 8.81-8.77 (br, 4H), 8.34-8.28 (br, 4H), 8.02-7.96 (br, 4H), 7.79-7.74 (br, 4H), 4.84-4.64 (br, 11H), 3.29 (s, 8H), 2.23-2.21 (t, 4H), 2.02-1.99 (m, 8H), 1.41-0.78 (br, 103H).

3. NMR

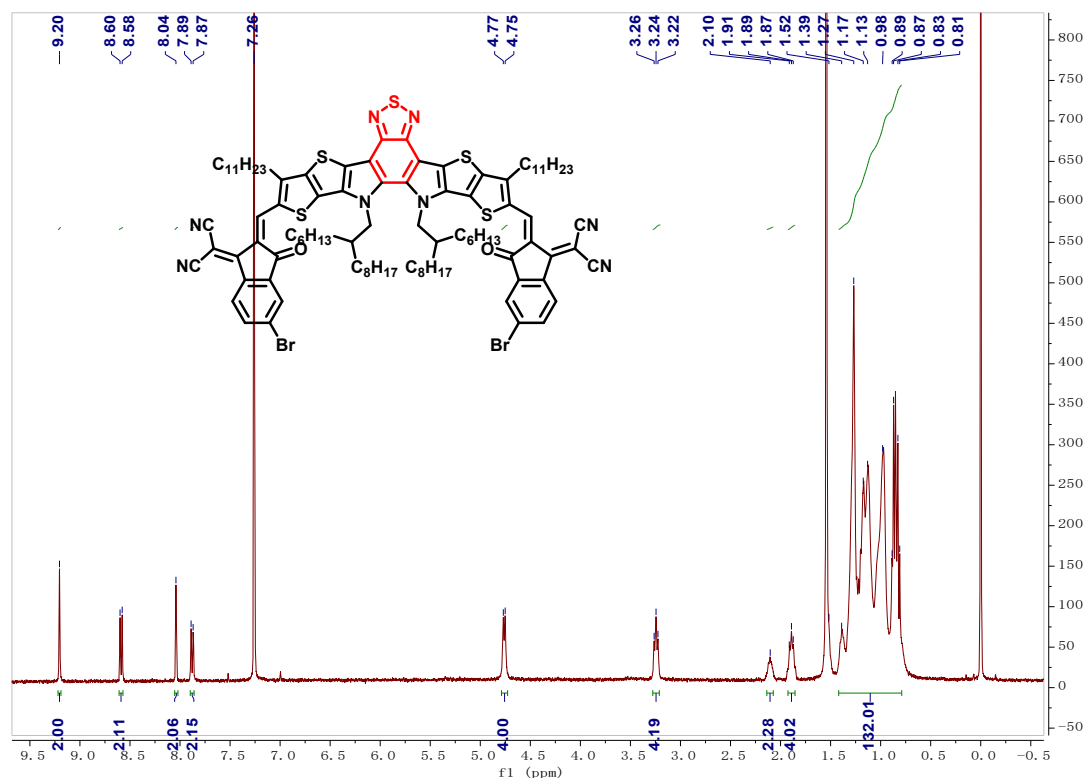


Figure S1. ¹H NMR spectrum of compound **YIC-Br- γ** (400 MHz, CDCl₃).

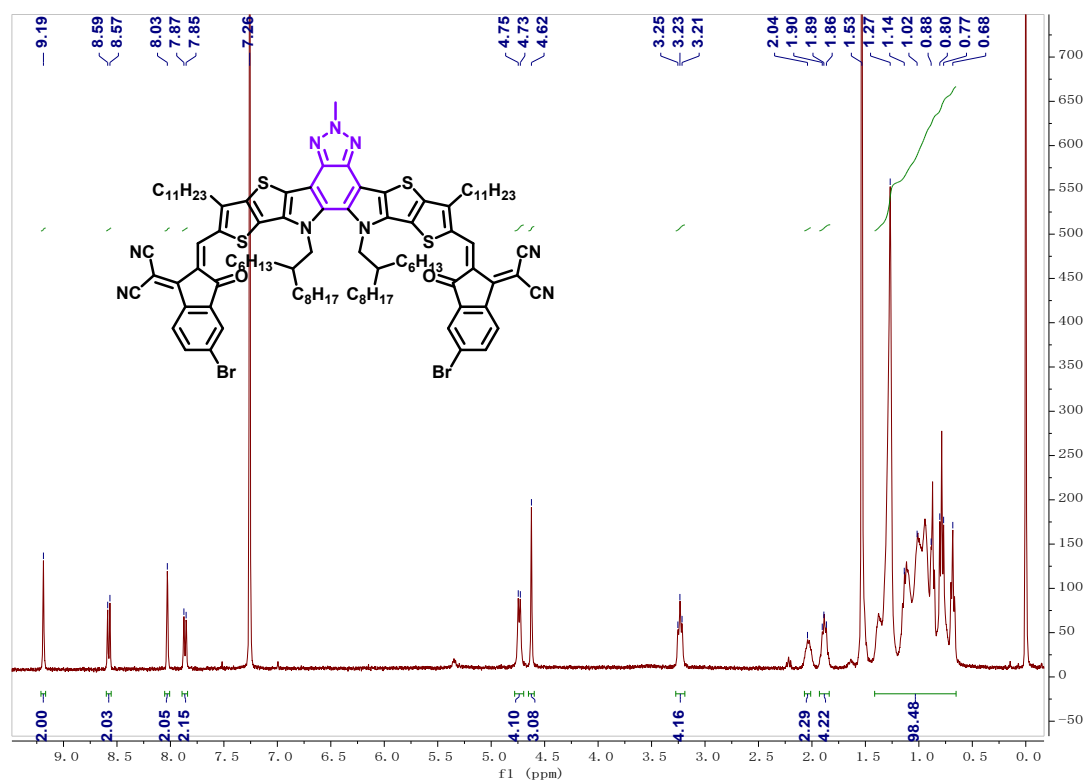


Figure S2. ^1H NMR spectrum of compound **ZIC-Br- γ** (400 MHz, CDCl_3).

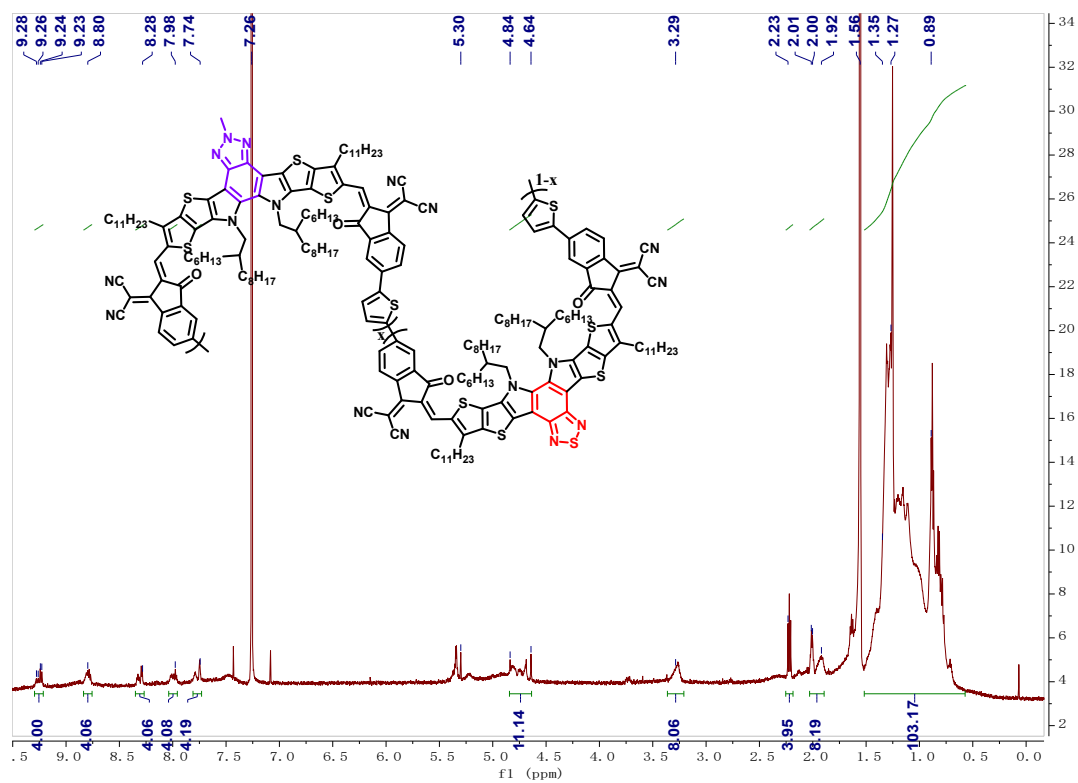


Figure S3. ^1H NMR spectrum of compound **P50- γ** (600 MHz, CDCl_3).

4. Device Fabrication and characterization

Conventional solar cells

PSMA-based polymer solar cells (PSCs) with a device structure of ITO/PEDOT:PSS/active layer/PFN-Br/Ag were fabricated under conditions as follows: the patterned ITO-coated glass was cleaned inside an ultrasonic bath by using deionized water, acetone, and isopropyl alcohol sequentially and dried in an oven at 90 °C. Before use, the ITO-coated glass substrates were treated in a UV-zone (Ming Heng, PDC-MG) for 20 min to improve their work function and clearance. A thin PEDOT:PSS (Heraeus Clevis P VP A 4083, filtered at 0.45 μm) layer (30 nm) was spin-coated onto the ITO substrates and then dried at 150 °C for 15 min in air. The PEDOT:PSS coated ITO substrates were fast transferred to an N_2 -filled glove box for further processing. To obtain the optimal device fabrication conditions for P50- γ , donor/acceptor (D/A) weight ratio, the processing solvent, additive volume ratio, and post-treatment were systematically optimized, as shown in Table S2 and figureS8. For all-PSCs based on PBDB-T:P50- γ blend, the optimal conditions were a D/A weight ratio of 1:1, CF as the solvent (PBDB-T concentration was fixed at 5.5 mg mL^{-1}) with the addition of 2.5% v/v chloronaphthalene (CN), and thermal annealing at 100 °C for 10 min. The active layer thicknesses were ~ 100 nm measured by a KLA Tencor D-100 profilometer. Then a methanol solution of poly[(9,9-bis(3'-(N,N-dimethyl)nethylammoniumpropyl)-2,7-fluorene) -alt-2,7-(9,9-dioctylfluorene)]dibromide (PFN-Br) at a concentration of 0.5 mg mL^{-1} was spin-coated on top of the active layer at 2000 r.p.m. for 30 s. Finally, a 120 nm Ag electrode was deposited on top of the active layers through a shadow mask under a vacuum of about 2×10^{-4} Pa. The active area was 5.7 mm^2 . The current-voltage (J - V) characteristic curves of all packaged devices were measured by using a Keithley 2400 Source Meter. Photocurrent was measured under AM 1.5G (100 mW cm^{-2}) using a Newport solar simulator (Newport model 94021A, 100 mW cm^{-2}). The light intensity was calibrated using a monocrystal silicon cell (VLSI Standards Inc.) to bring spectral mismatch to unity. The EQE was obtained by Solar Cell Spectral Response Measurement System QE-R3018 (Enli Technology Co., Ltd.) and a standard Si

photovoltaic cell was employed to calibrate the light intensity.

Hole- and electron-only devices

The hole mobility was measured in a hole-only device composed of ITO/PEDOT:PSS/active layer/MoO₃/Ag. The electron mobility was measured in an electron-only device composed of ITO/ZnO/acceptor pure films or active layer/PFN-Br/Ag. The active layers were spin-coated on ITO substrates covered with 40 nm PEDOT:PSS for the hole-only device. The active layers were prepared according to the fabrication process of the all-PSCs. After that, MoO₃ (10 nm) and Ag (120 nm) were vacuum-deposited on the active layer as the cathode. For the electron-only device, the blend films were spin-coated on ITO substrates covered with a layer of ZnO (40 nm). The active layers and PFN-Br were prepared according to the fabrication process of the all-PSCs. After that, Ag (120 nm) was vacuum-deposited on the active layer as the cathode. The charge mobility was determined by fitting the dark current to the space-charge-limit current (SCLC) model of a single carrier SCLC, described by the Equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu(V_{appl} - V_{bi})^2}{8L^3}$$

Where J is the current density of the hole-only or electron-only devices, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, μ is the mobility, V_{appl} is the applied voltage, V_{bi} is the built-in voltage and L is the thickness of the active layer.

5. GPC measurements

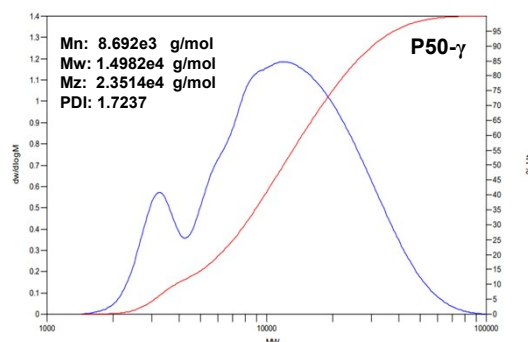


Figure S4. GPC results for P50- γ .

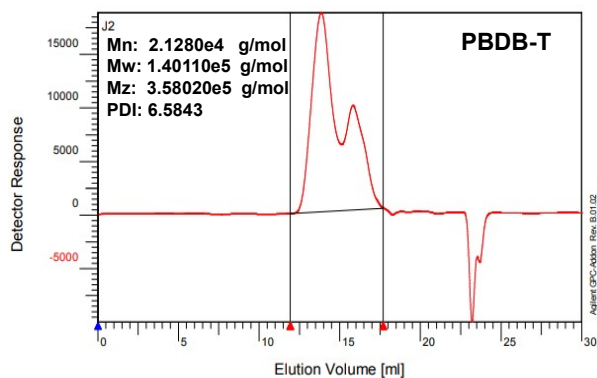


Figure S5. GPC results for PBDB-T.

6. TGA and DSC measurements

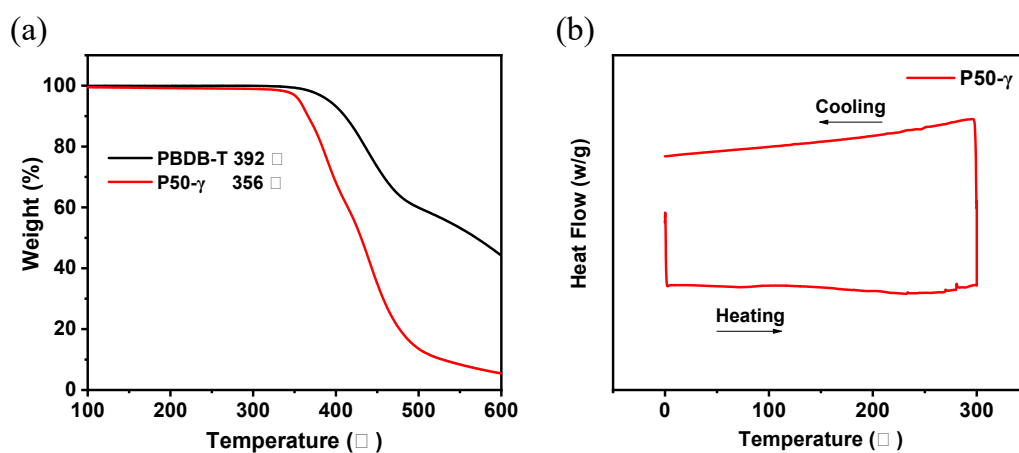


Figure S6. (a) TGA curves of P50- γ and PBDB-T. (b) DSC curves of P50- γ .

7. PBDB-T *UV-vis* measurement

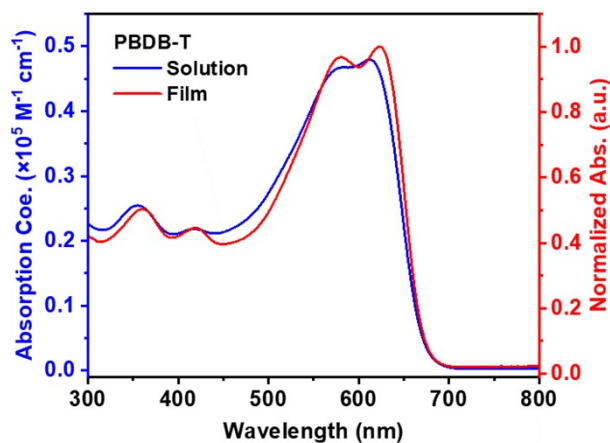


Figure S7. Absorption spectra of PBDB-T in dilute chloroform and thin film.

8. Cyclic voltammetry (CV) measurements

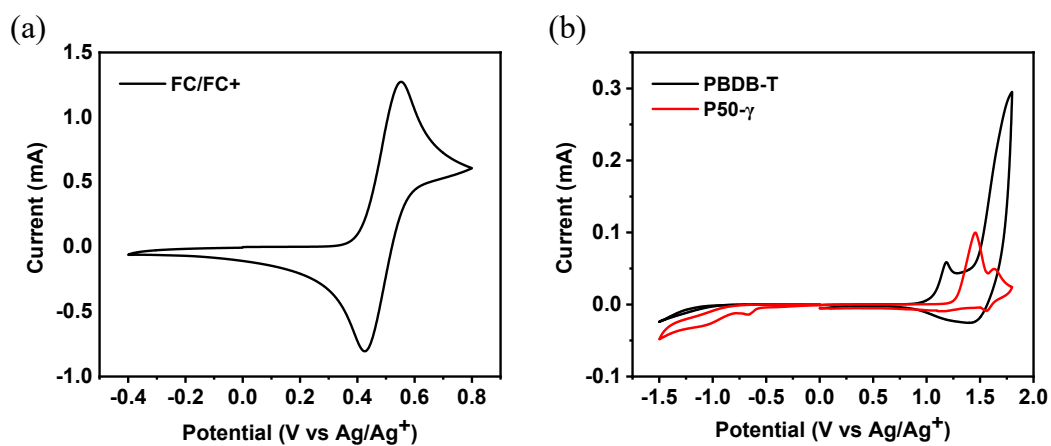


Figure S8. Cyclic voltammograms of (a) ferrocene (b) PBDB-T and P50- γ .

9. GIWAXS measurements

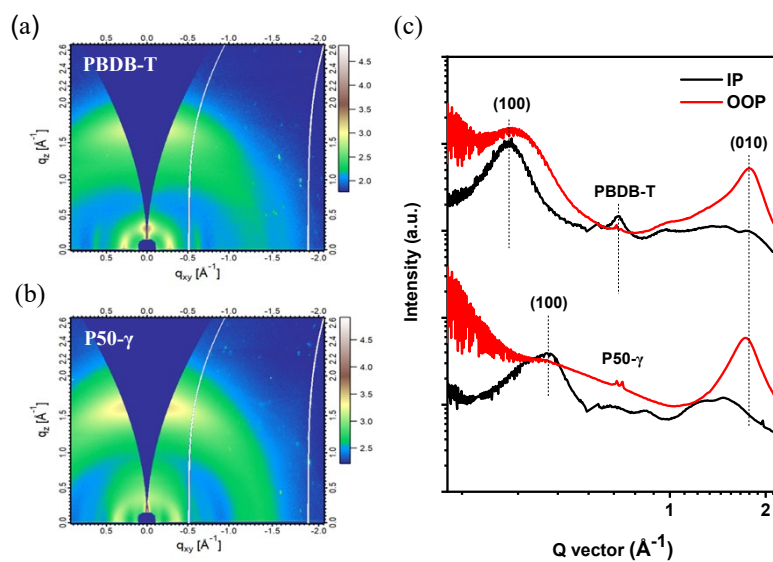


Figure S9. (a-b) 2D GIWAXS pattern and (c) scattering profile for neat PBDB-T and P50- γ film.

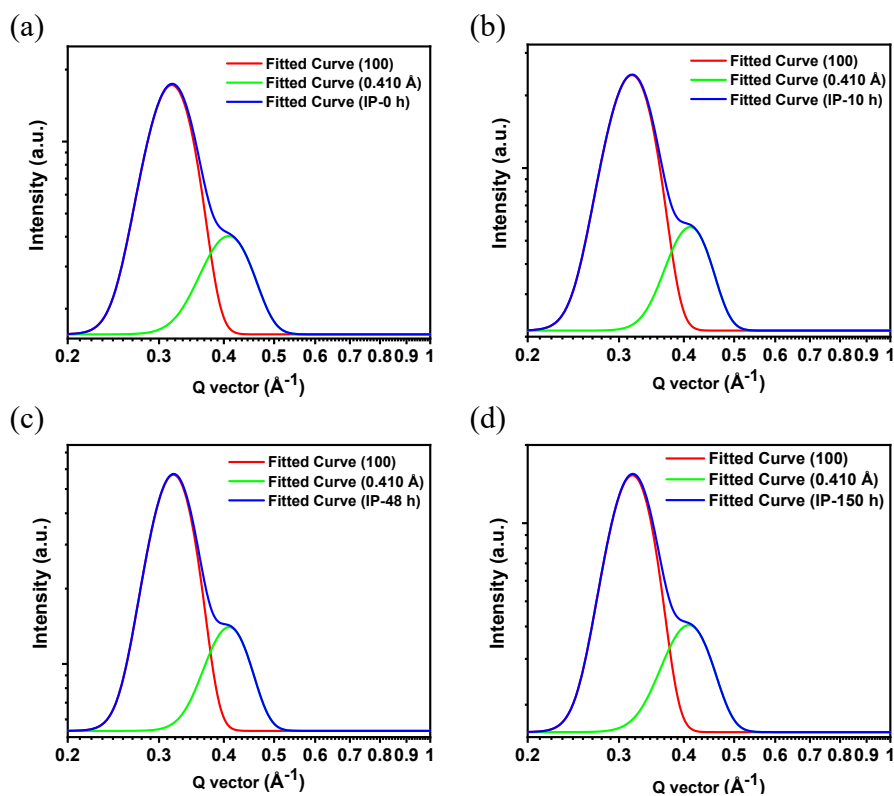


Figure S10. (a) Pristine and (b-d) different annealing times the blend films multiple peak splitting fits of the IP (100) direction.

Table S1. Summary of the parameters for the neat and blended films obtained from the GIWAXS measurements.

Materials	In plane				Out of plane			
	Location (\AA^{-1})	d-spacing (\AA)	FWHM	CCL (\AA)	Location (\AA^{-1})	d-spacing (\AA)	FWHM	CCL (\AA)
PBDB-T	0.318	19.7	0.084	67.5	1.780	3.5	0.444	12.9
	0.692	9.1	0.112	50.8				
P50- γ	0.392	16.0	0.058	97.5	1.727	3.6	0.384	14.9
PBDB-T:P50- γ (Pristine)	0.318	19.7	0.060	94.4	1.769	3.6	0.376	15.2
	0.410	15.3	0.124	45.6				
	0.687	9.1	0.107	52.9				
PBDB-T:P50- γ (10 h @80 $^{\circ}\text{C}$)	0.318	19.7	0.059	95.9	1.769	3.6	0.370	15.5
	0.410	15.3	0.128	44.3				

	0.687	9.1	0.111	51.2				
PBDB-T:P50- γ (48 h @80 °C)	0.318	19.7	0.060	94.4	1.769	3.6	0.382	15.0
	0.410	15.3	0.132	42.8				
	0.687	9.1	0.125	45.3				
PBDB-T:P50- γ (150h @80 °C)	0.318	19.7	0.060	94.9	1.769	3.6	0.398	14.4
	0.410	15.3	0.140	40.4				
	0.687	9.1	0.150	37.8				

10. Optimization of device performance

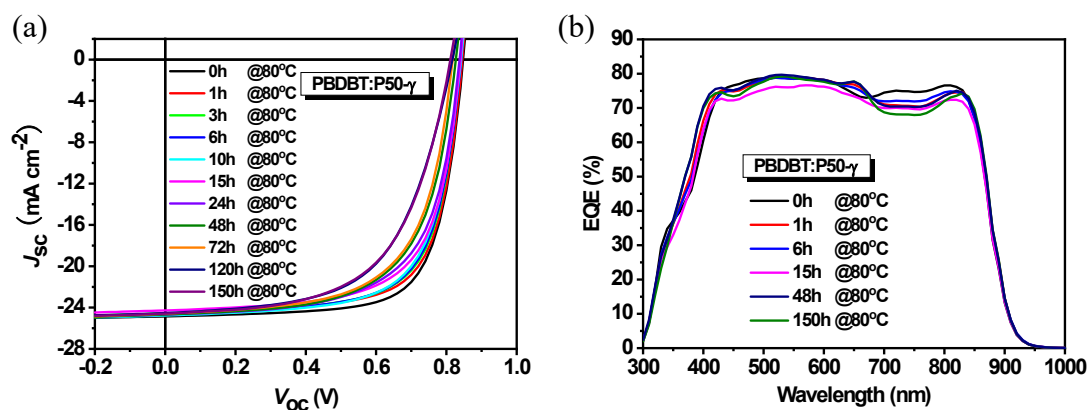


Fig. S11 (a) J - V curves and (b) EQE spectra for P50- γ -based PSCs.

Table S2. Photovoltaic data of the PBDBT:P50- γ -based PSCs after prolonged heating at 80 °C.

Annealing Time (h)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%) ^a
0	0.85	24.85	71.65	15.10
1	0.85	24.64	70.06	14.60
3	0.84	24.55	69.40	14.33
6	0.84	24.60	68.75	14.26
10	0.84	24.77	67.88	14.16
15	0.84	24.26	67.00	13.66
24	0.84	24.67	64.36	13.30

48	0.83	24.66	63.60	12.98
72	0.82	24.58	63.58	12.78
120	0.82	24.53	59.15	11.86
150	0.81	24.58	59.08	11.79

^a Average value in brackets was obtained from 10 devices.

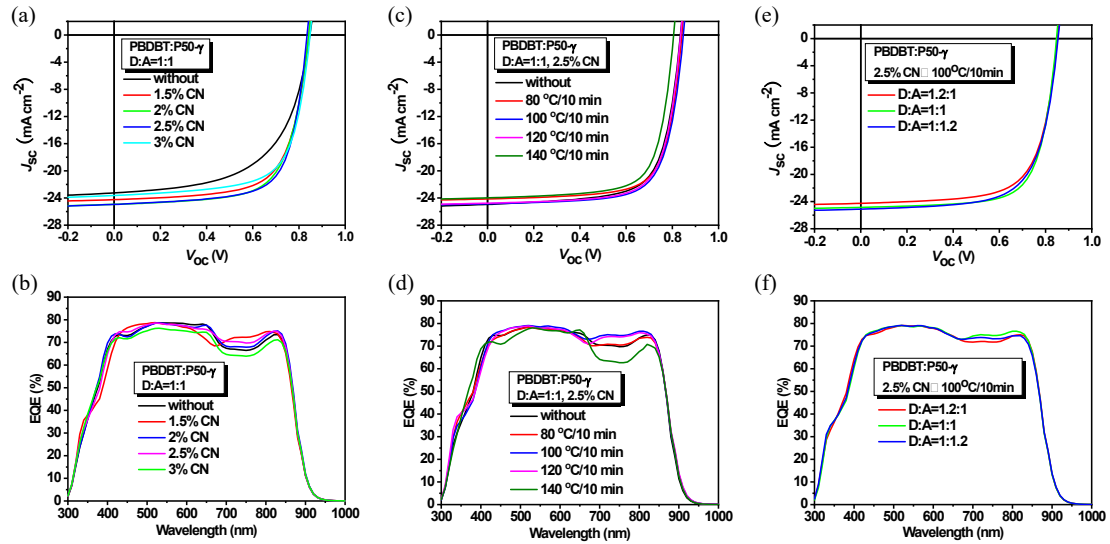


Fig. S12 (a-b) $J-V$ curves and EQE spectra based on PBDB-T:P50- γ (w/w, 1:1) with different content (v/v) chloronaphthalene as additives. (c-d) $J-V$ curves and EQE spectra based on PBDB-T:P50- γ (w/w, 1:1; v/v, 2.5% CN) with different thermal annealing temperatures. (e-f) $J-V$ curves and EQE spectra based on PBDB-T:P50- γ (v/v, 2.5% CN; 100 °C/10 min) with different D:A weight (w/w) ratios.

Table S3. Photovoltaic data of the PSMA-based PSCs based on PBDB-T:P50- γ with the different conditions under the illumination of AM 1.5G, 100 mW cm⁻²

PBDB-T:P50- γ	Condition	V_{oc} (V)	J_{sc} (mA/cm ²)	$J_{SC,EQE}$ (mA/cm ²)	FF (%)	PCE (%)
Solvent Additive	without	0.85	23.25	23.39	58.43	11.51
	1.5%CN	0.84	24.24	23.46	68.10	13.92
	2.0%CN	0.84	24.94	23.59	68.35	14.36
	2.5%CN	0.85	24.94	23.64	70.28	14.64
	3.0%CN	0.85	23.63	22.68	68.56	13.75

Thermal Annealing	without	0.85	24.94	23.64	70.28	14.64
	80°C/10min	0.84	24.13	23.57	72.25	14.67
	100°C/10min	0.85	24.85	24.11	71.65	15.10
	120°C/10min	0.84	24.75	23.92	71.98	14.90
	140°C/10min	0.81	23.98	22.86	72.05	13.93
D:A (Weight Ratio)	1.2:1	0.85	24.25	24.11	69.12	14.28
	1:1	0.85	24.85	24.11	71.65	15.10
	1:1.2	0.85	25.10	24.11	68.36	14.66

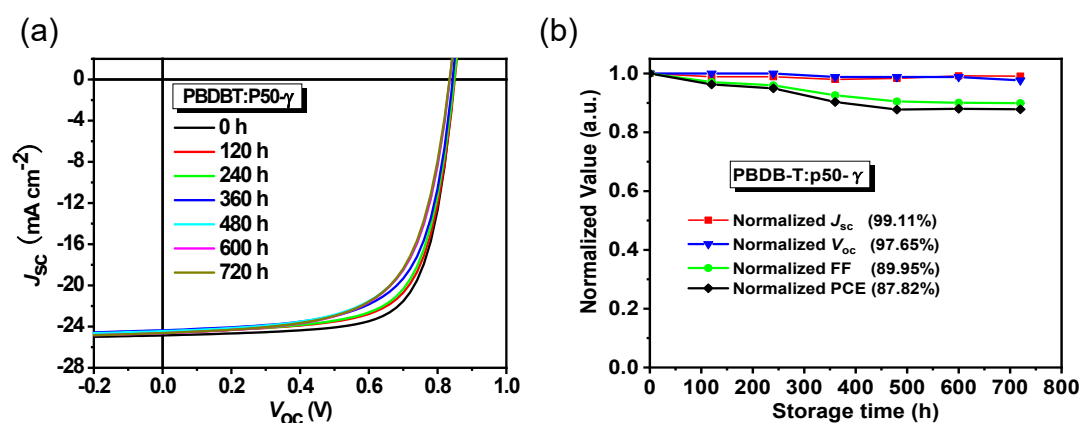


Fig. S13 (a) J - V curves and (b) variation of normalized J_{SC} , V_{OC} , FF, and PCE losses based on PBDB-T:P50- γ (w/w, 1:1; v/v, 2.5% CN; 100 °C/10 min) with different storage times in the N_2 -filled glovebox.

Table S4. Photovoltaic Data of the PSMA-based PSCs Based on PBDB-T:P50- γ (w/w, 1:1; v/v, 2.5% CN; 100 °C/10 min) with different storage times in the N_2 -filled glovebox.

Storage Time (h)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
0	0.85	24.85	71.65	15.10
120	0.85	24.58	69.56	14.54
240	0.85	24.58	68.76	14.34
360	0.84	24.35	66.36	13.64
480	0.84	24.44	64.84	13.25
600	0.84	24.65	64.52	13.29

11. SCLC measurements for PBDB-T, P50- γ , and PBDB-T:P50- γ blend films

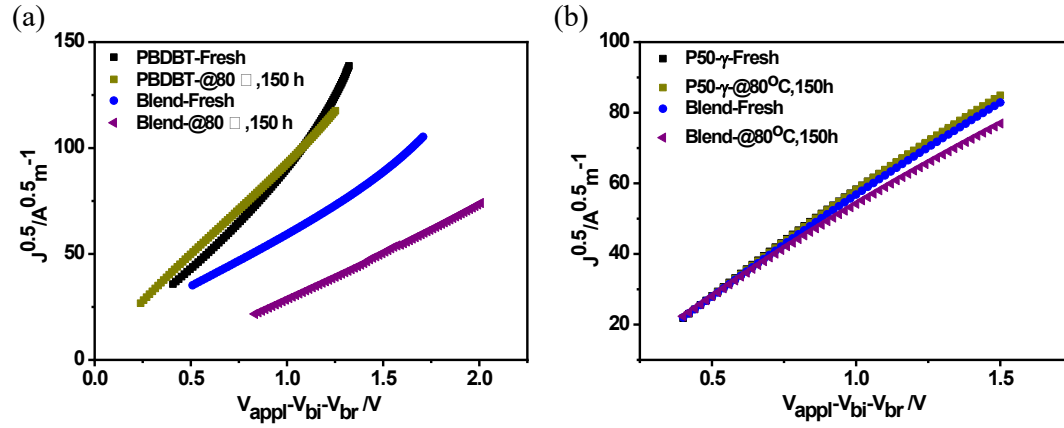


Fig. S14 The experimental current density-applied voltage characteristics for (a) hole-only and (b) electron-only devices

Table S5. The electron and hole mobility results are measured by the SCLC method.

Devices	μ_e ($\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	μ_h ($\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	μ_e / μ_h
P50- γ (fresh)	9.91	—	—
P50- γ (80 °C, 150 h)	8.03	—	—
PBDBT (fresh)	—	29.53	—
PBDBT (80 °C, 150 h)	—	18.45	—
Blend (fresh)	8.64	8.49	1.02
Blend (80 °C, 150 h)	6.64	4.72	1.41

Reference

1. J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li and Y. Zou, *Joule*, 2019, **3**, 1140-1151.
2. H. Fu, Y. Li, J. Yuan, Z. Wu, Q. Fan, F. R. Li, H. Y. Woo, F. Gao, Z. Zhu and A. K. Jen, *J. Am. Chem. Soc.*, 2021, **143**, 2665-2770.