Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

# Supplementary Information

## 1. Experimental Section

*Materials:* The polymer donors PBDB-T was purchased from Solarmer Materials Inc, non-fullerene polymer acceptors PYTT-1, PYTT-2 and PYTT-3 were synthesized in our group according to our previously reported work.[1] Solvents (chloroform) was dried and distilled from appropriate drying agents prior to use.

*Device Fabrications and Testing:* For the measurement of device performance and stability, the conventional devices were fabricated with a structure of ITO/PEDOT:PSS/active layer/PDINN/Ag. Patterned ITO substrates were cleaned with methylbenzene, deionized water, acetone and isopropyl alcohol in an ultrasonic bath for 10 min each. After drying and procesed in ultraviolet-ozone chamber for 15 min, a thin layer of PEDOT:PSS (poly(3,4-ethylene dioxythiophene): poly(styrenesulfonate)) was deposited through spin-coating on ITO-coated glass a the speed of 4000rpm for 30 s, following by thermal annealing at 150 °C for 15 minutes in air. Then the active layer was spin-coated in a $N_2$-filled glovebox from PBDB-T:PYTT-$x$ ($x$ = 1-3) polymer acceptors blend solution in chloroform (1:1.5, wt%; 15 mg/ml; 3 vol % 1-chloronaphth alene (CN) as the additive) on PEDOT:PSS layer. After that, the active layers were annealed at 100 °C for 10 min. The PDINN was dissolved in methanol with a concentration of 1.0 mg mL$^{-1}$ and then was deposited the top of active layer. Finally, 100 nm of silver (Ag) were thermally evaporated through a mask under a vacuum of ~ $5\times10^{-6}$ mbar to complete the fabrication of the devices. The current-voltage characteristics of the solar cells were measured in the $N_2$-filled glovebox under AM 1.5G irradiation (100 mW cm$^{-2}$) on an Enli Solar simulator (made by Enli Technology Co., Ltd., Taiwan, calibrated by The National Institute of Metrology (NIM) of China).

*Film Fabrication:* Before the spin coating of solution, the quartz glasses were cleaned by ultrasonic treatment in water, acetone and isopropanol for 30min, respectively. The films were then deposited by the spin-coated of blend CF solution on the cleaned quartz substrates, which then followed the same procedure that was applied for device fabrication but without the process of deposit of PDINN and Ag electrode.

*Stability test*: The devices were encapsulated by glass slides using epoxy in an $N_2$-filled glovebox before stability test. All the fabrication process is consistent with what is mentioned above. The *J-V* characteristic was monitored by the *I-V* test system and kept at the MPP at the interval of the test. An array of white LEDs was used as light source with intensity equivalent to one sun. Hole-only and electron-only devices were fabricated and aged under the same condition as the solar cells. And the light-soaking tests were calibrated by the light meter (TES-1332A, TES Electrical Electronic Corp.).

*Film Measurements*: A Perkin Elmer Lambda-365 absorption spectrometer with the spectrum ranging from 300 nm to 1100 nm was used to determine the steady-state absorbance attenuation periodically. Atomic Force Microscopy (AFM) images were obtained by using Nano Wizard 4 atomic force microscopy (JPK Inc. Germany) in Qi mode to observe the surface morphologies of films deposited on glass substrates. FTIR spectra were measured on a VERTEX70 (Bruker Optik GmbH/Germany) infrared spectrometer with wavenumber ranging from 400 to 4000 $cm^{-1}$, the samples were drop-cast onto KBr substrate and then thermal annealing of 100℃ for 10mins. Photoluminescence (PL) data were collected using a Zolix Flex One Spectrometer equipped with 532 nm and 639nm laser excitation, The luminescence spectra were recorded with Si CCD or InGaAs detector according to the material feature. Contact angle measurements were performed on contact angle measurement system (Attension Theta Lite) using water or ethylene glycol as the wetting liquid, surface energy values, calculated with the OWRK model, for the different samples.

*The GIWAXS and GISAXS measurements*: Grazing-incidence wide-angle and small-angle X-ray scattering (GIWAXS/GISAXS) measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2°.

*Device Measurements*: The Electroluminescence (EL) measurements were performed with same setup for PL measurement. The EL signal was stimulated by applying an external voltage/current source from Keithly2400 through the devices.

*Transient photocurrent (TPC) measurements*: The solar cell was held at short-circuit conditions ($R_{load}$ = 50 Ω), while it is illuminated with a constant light bias from high power LED powered by Keithley 2200-20-5. An intense short laser pulse (405 nm laser diode connected to a Keysight 33500B wavefunction generator) generates a small perturbation charge. The current traces were recorded on a Keysight DSOX2024A digital storage oscilloscope by measuring the voltage drop.

*Transient Photovoltage (TPV) Measurements*: The device was held at open circuit ($R_{load}$ = 1 MΩ) under steady state conditions controlled by a continuous white light bias (Keithley 2200-20-5 programmable power supply for powering the high power LED) and a 405 nm laser diode (Keysight 33500B) is applied to generate an additional amount of charges causing a small voltage perturbation below 10mV (recorded by Keysight DSOX2024A). After the pulse, the voltage decays back to its steady-state value in a single exponential decay. The characteristic decay time was determined from the linear fit to a logarithmic plot of voltage transient and returned the small perturbation charge carrier lifetime.

*Measurements of Photo-CELIV*: Photo-induced charge carrier extraction by linearly increasing voltage measurements were taken with a 405-nm laser diode as the illumination source. Current transits were recorded across an internal 50 Ω resistor on an oscilloscope (Keysight DSOX2024A). A fast electrical switch was applied to isolate the device in order to prevent carrier extraction or sweep out during the laser pulse and delay time. After the variable delay time, a linear extraction ramp (3 V in amplitude and 60 µs long) was applied via a function generator after a variable delay time. To investigate the carrier mobility in the corresponding devices, the Photo-CELIV curves were conducted using different experimental conditions, differing in delay time and applied voltage.

*Capacitance spectroscopy*: Capacitance spectroscopy measurements were performed with an impedance analyzer in the ModuLab XM electrochemical workstation (AMETEK, UK) in the dark and under one sun AM 1.5G illumination. The detailed data analysis was depicted elsewhere.[2,3]

## 2. Figures and Tables

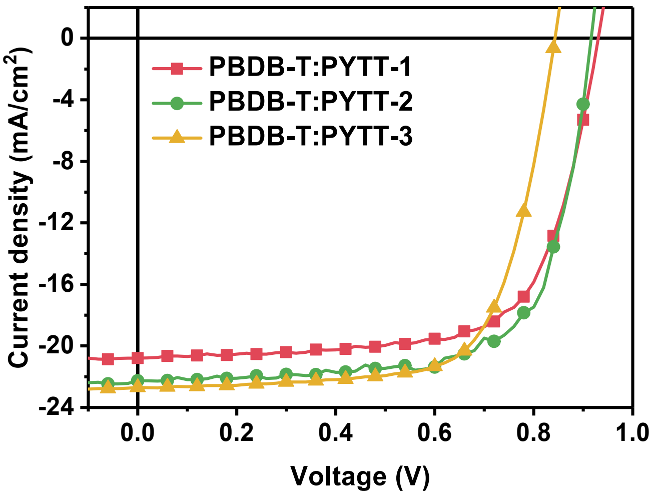

**Figure S1**. The current-voltage (*J-V*) curves of the PBDB-T: PYTT-*x* (*x*=1-3)-based devices.

**Table S1**. Photovoltaic parameters of OSCs based on PBDB-T as the donor and studied acceptors under the illumination of AM 1.5G, 100 mW cm$^{-2}$.

| Acceptors | Molecular weights ($Mw$) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%)$^a$ |
|---|---|---|---|---|---|
| PYTT-1 | 18.3 kDa | 0.930 | 20.71 | 69.35 | 13.36 (13.29±0.07) |
| PYTT-2 | 17.1 kDa | 0.916 | 22.26 | 70.45 | 14.35 (14.23±0.12) |

| | | | | | |
|---|---|---|---|---|---|
| PYTT-3 | 15.6 kDa | 0.843 | 22.70 | 70.08 | 13.41 (13.32±0.09) |

a) Values in the parenthesis are the average PCEs based on eight devices

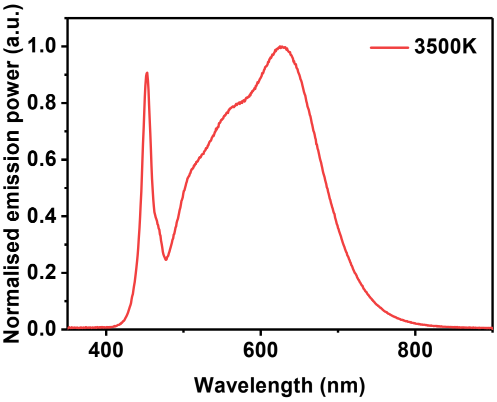

**Figure S2**. Spectra of white LED used for degradation test.

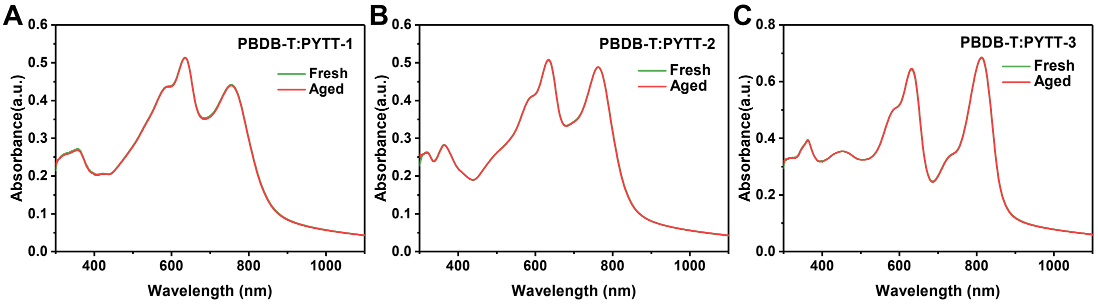

**Figure S3**. The comparison of absorption of fresh and aged blend films based on polymer acceptors (A) PYTT-1, (B) PYTT-2, and (C) PYTT-3 mixed with polymer donors PBDB-T.

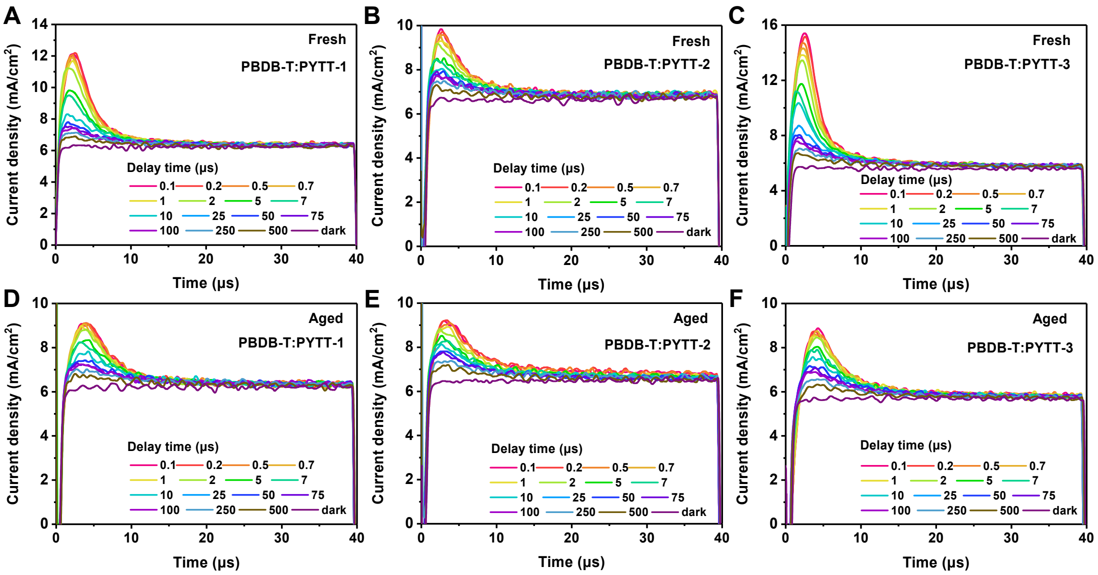

**Figure S4**. Photo-CELIV traces of fresh and aged solar cell based on PYTT-1, PYTT-2, and PYTT-3 device as a function of delay time.

**Table S2.** Calculated mobility (unit = cm$^2$ V$^{-1}$ s$^{-1}$) from Photo-CELIV measurements and SCLC.

| Acceptors | Mobility from Photo-CELIV[a] | | Hole[b] | | Electron | |
|---|---|---|---|---|---|---|
| | Fresh | Aged | Fresh | Aged | Fresh | Aged |
| PYTT-1 | $1.60\times10^{-4}$ | $5.53\times10^{-5}$ | $2.50\times10^{-4}$ | $1.87\times10^{-4}$ | $3.95\times10^{-4}$ | $1.61\times10^{-4}$ |
| PYTT-2 | $1.17\times10^{-4}$ | $9.03\times10^{-5}$ | $2.90\times10^{-4}$ | $2.65\times10^{-4}$ | $2.71\times10^{-4}$ | $1.89\times10^{-4}$ |
| PYTT-3 | $1.80\times10^{-4}$ | $5.47\times10^{-5}$ | $2.79\times10^{-4}$ | $1.82\times10^{-4}$ | $4.10\times10^{-4}$ | $1.01\times10^{-4}$ |

[a] The charge carrier mobility is calculated for different delay time according to the following equation:

$$\mu = \frac{2d^2}{3At_{max}^2\left[1 + 0.36\frac{\Delta j}{j(0)}\right]}(\Delta j \approx j(0))$$

. where *d* is the thickness of the device, *A* is the voltage rise speed, $t_{max}$ is the time at the maximum $\Delta j$ of the extraction peak, and *j(0)* is the displacement current of the capacitance.[4] The average mobility of all delay times is used for comparison and discussion.

[b] The electron-only and hole-only devices were fabricated following the structure of ITO/ZnO/Active layer/PDINN/Ag and ITO/PEDOT:PSS/Active layer/$MoO_3$/Ag respectively. The current density-voltage (*J-V*) characteristics of the hole or electron only devices were fitted by the following equation:

$$J_{SCL} = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V_{in}^2}{L^3}exp(\frac{0.89 \times \beta}{\sqrt{L}}\sqrt{V})$$

where $J_{SCL}$ is the current density, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative dielectric constant of the active layer and the value we used here is 3, $\mu$ is the mobility of electron, $L$ is the thickness of the active layer and $V_{in}$ is obtained from $V_{in}= V_{app}-V_{bi}-V_s$, where $V_{appl}$ is the applied voltage, $V_{bi}$ is the built-in voltage (0.3V), $V_s$ is the voltage drop from the substrate's series resistance ($V_s = IR$).

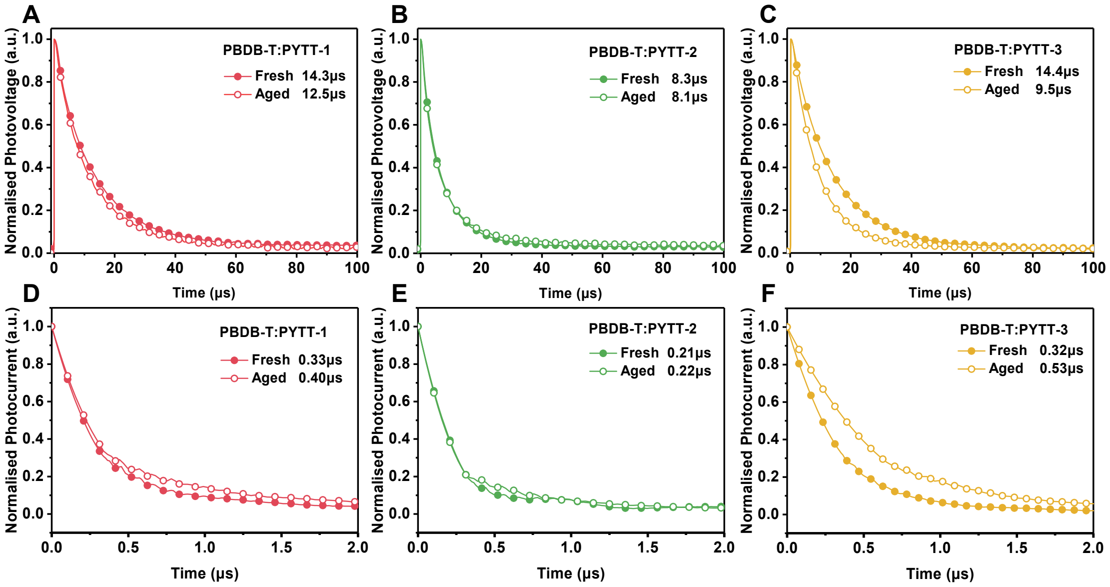

**Figure S5**. (A-C) transient photovoltage (TPV) and (D-F) transient photocurrent (TPC) measurement of fresh and aged solar cell based on PYTT-1, PYTT-2, and PYTT-3 device.

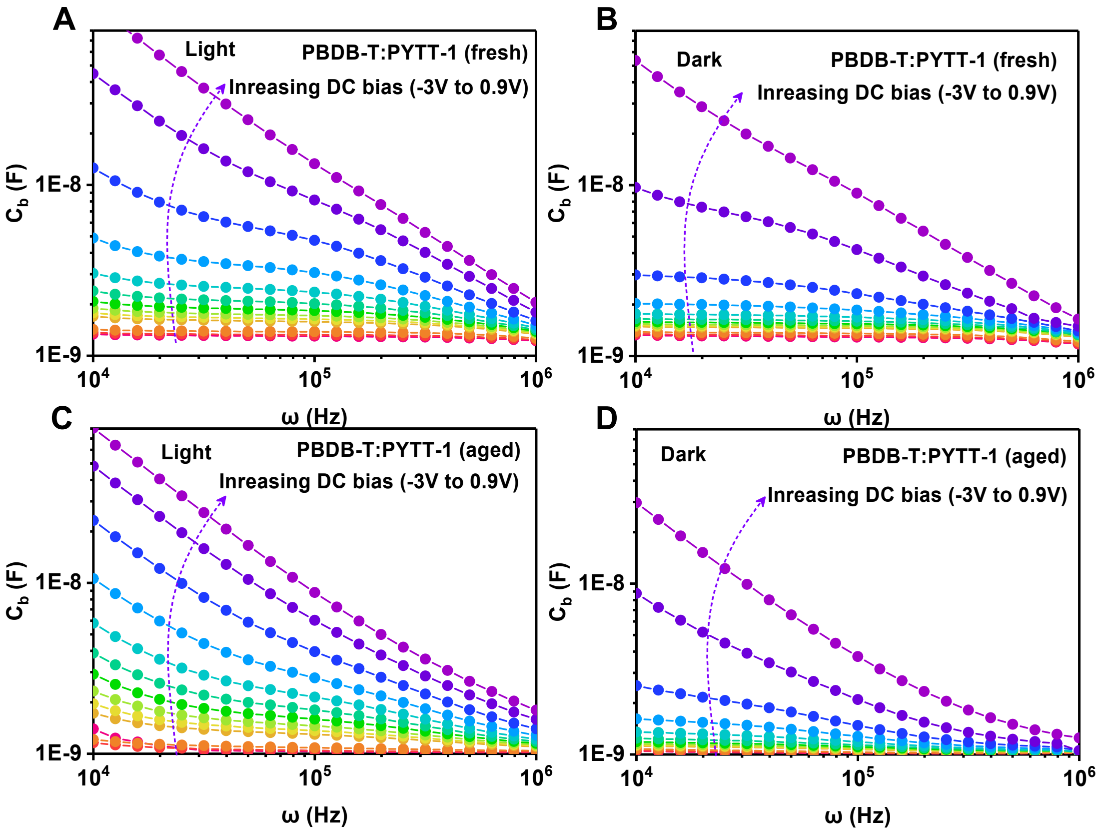

**Figure S6**. The capacitance spectra of the (A, B) fresh and (C, D) aged PBDB-T:PYTT-1 solar cell at different biases measured under 1 sun AM1.5G illumination or in the dark.

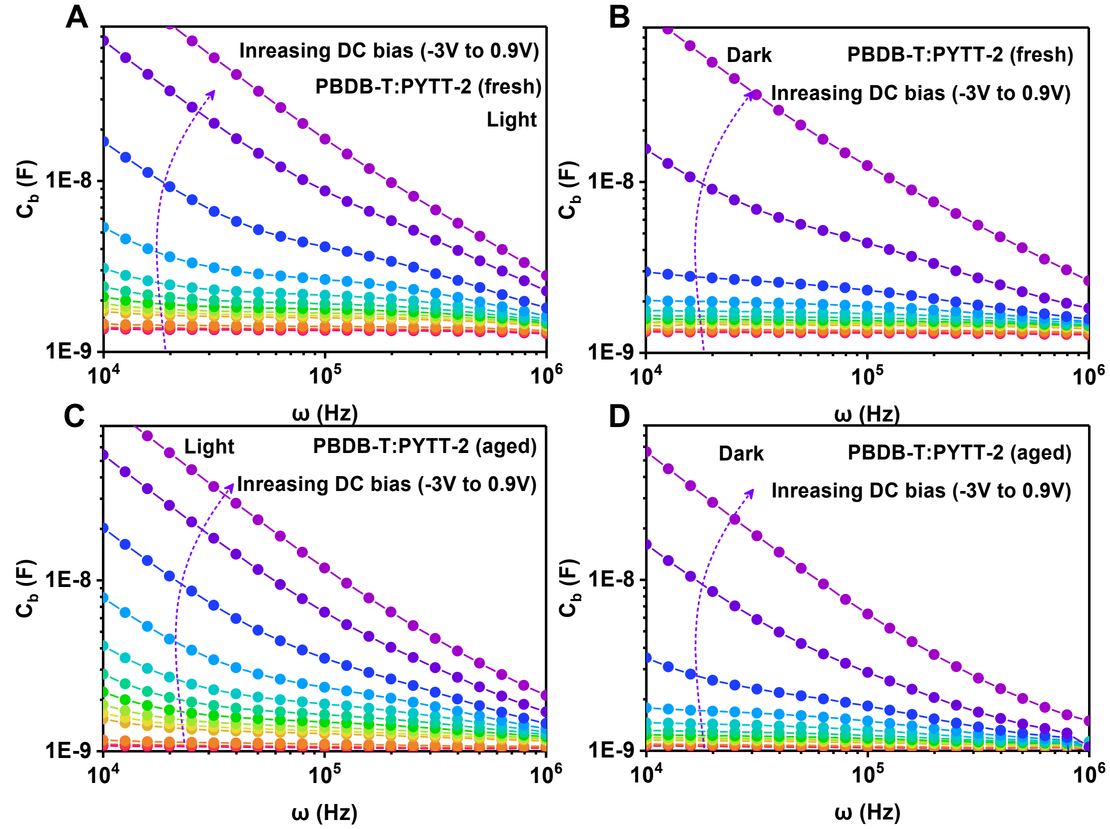

**Figure S7**. The capacitance spectra of the (A, B) fresh and (C, D) aged PBDB-T:PYTT-2 solar cell at different biases measured under 1 sun AM1.5G illumination or in the dark.

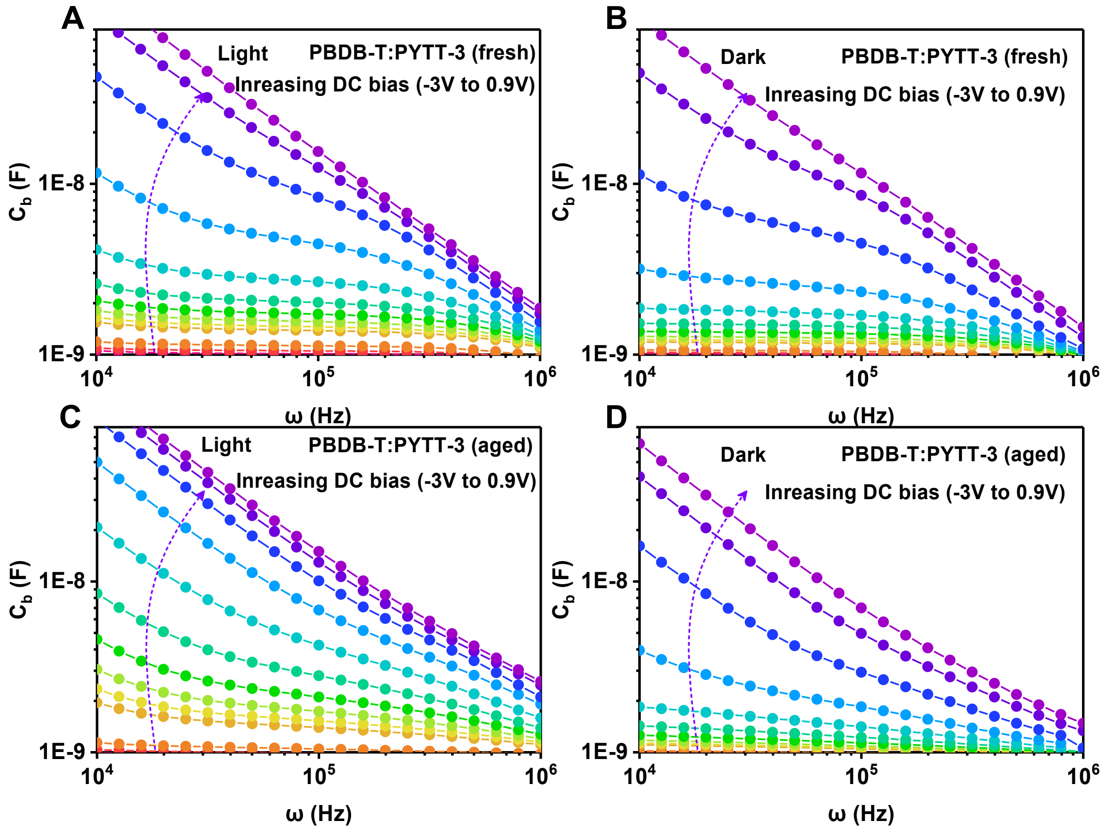

**Figure S8**. The capacitance spectra of the (A, B) fresh and (C, D) aged PBDB-T:PYTT-3 solar cell at different biases measured under 1 sun AM1.5G illumination or in the dark.

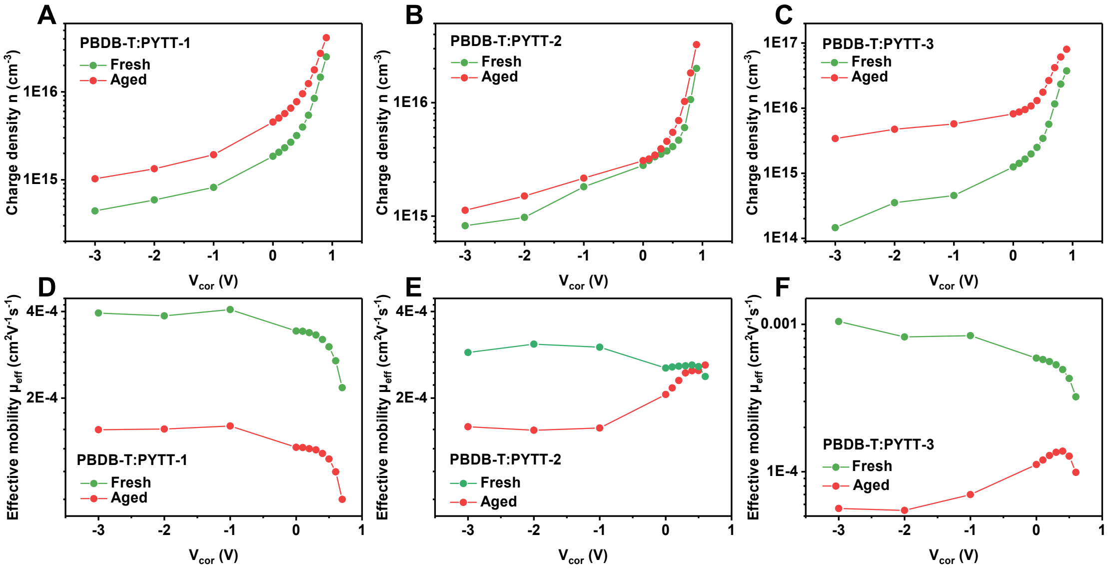

**Figure S9**. (A-C) Charge carrier density n and (D-F) effective mobility $\mu_{eff}$ of the solar cells based on polymer acceptors PYTT-1, PYTT-2, and PYTT-3.

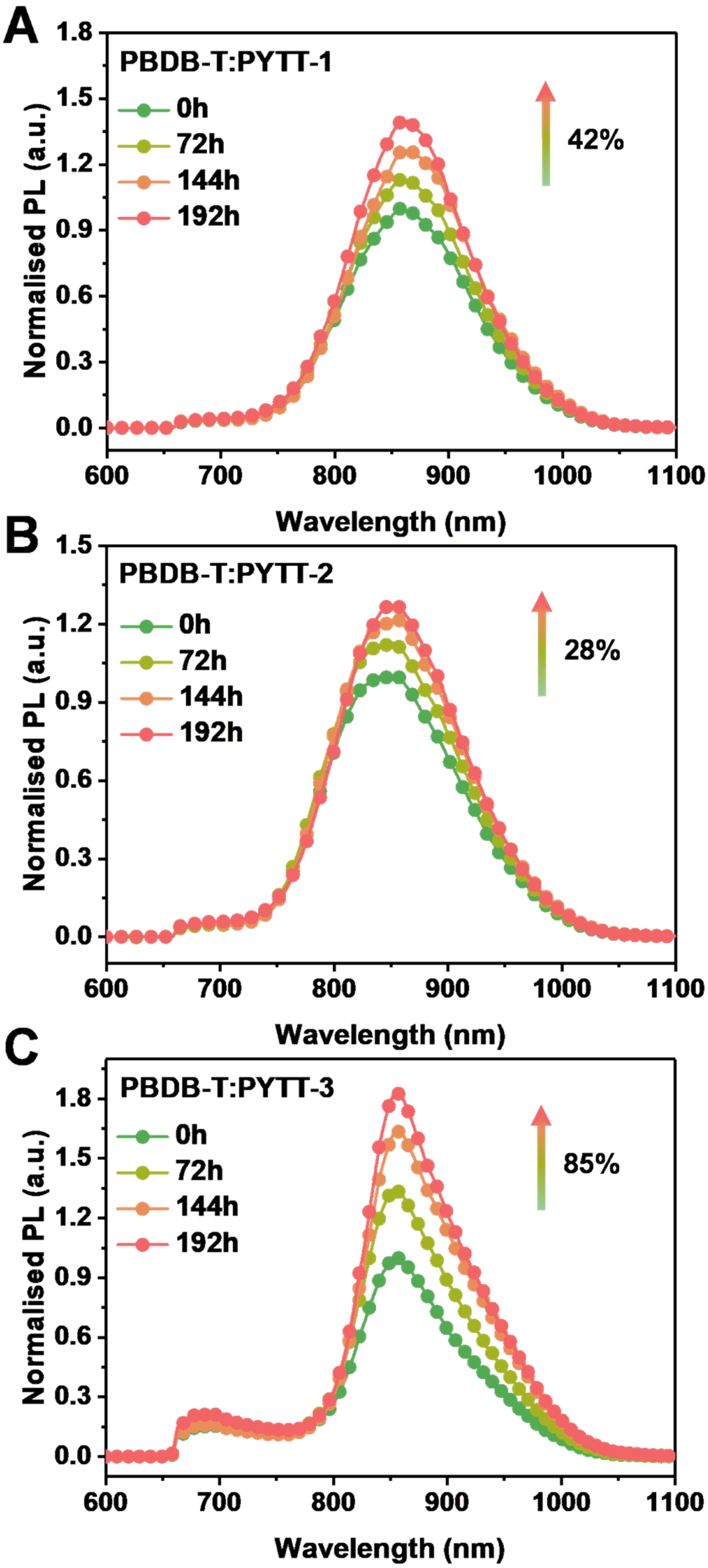

**Figure S10**. The temporal evolution of photoluminescence (PL) spectra for blend films based on different acceptors (A) PYTT-1, (B) PYTT-2, and (C) PYTT-3 blended with PBDB-T with various light-exposure periods.

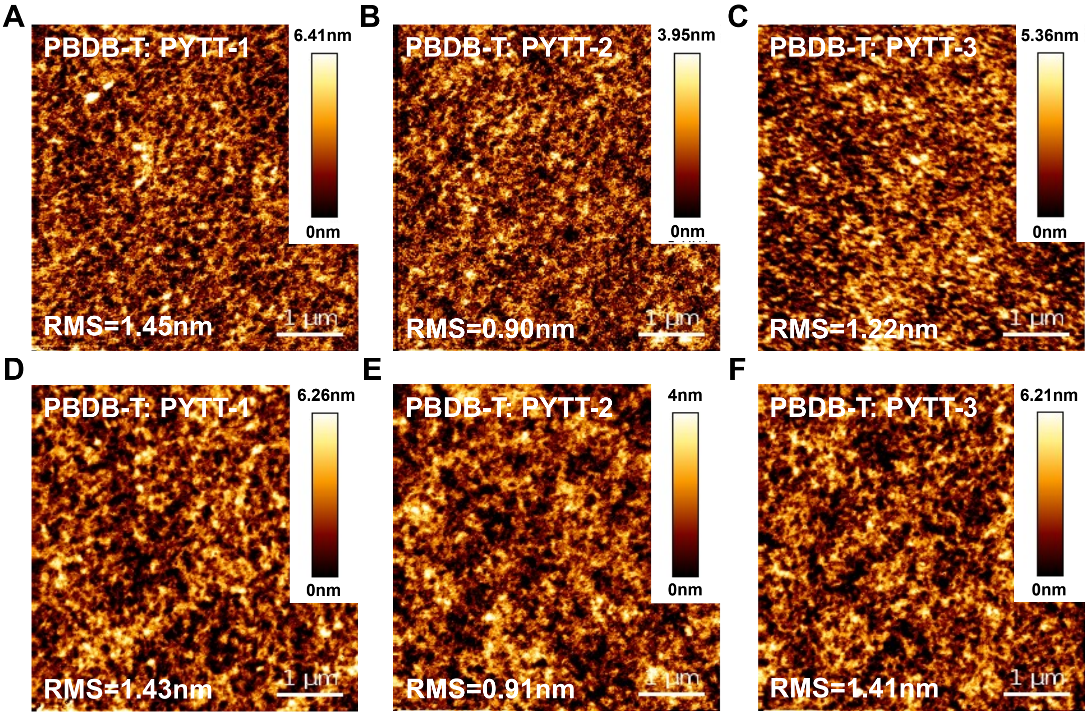

**Figure S11**. AFM image of fresh (Top row: A-C) and aged (Bottom row: D-F) blend films based on different acceptors (A, D) PYTT-1, (B, E) PYTT-2, and (C, F) PYTT-3 blended with PBDB-T.

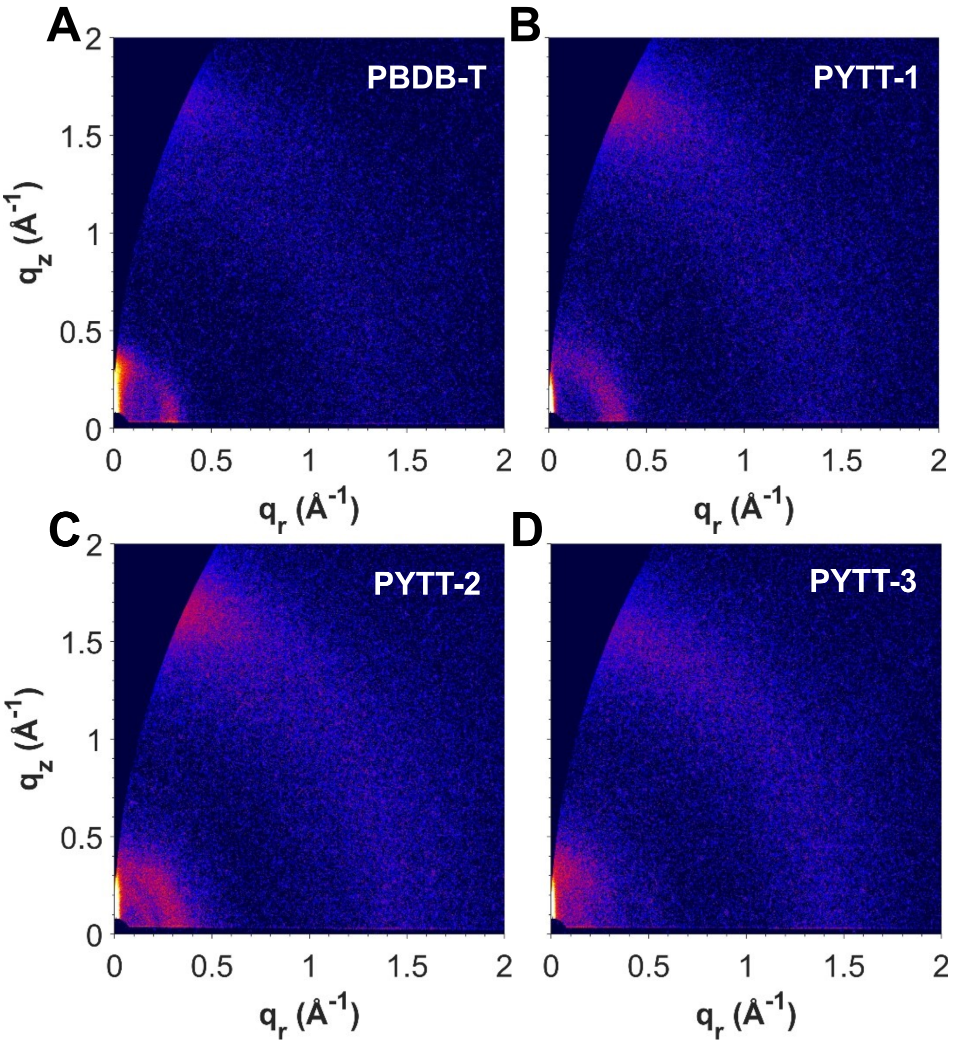

**Figure S12**. 2D GIWAXS patterns of pristine (A) PBDB-T, (B) PYTT-1, (C) PYTT-2, and (D) PYTT-3 films.

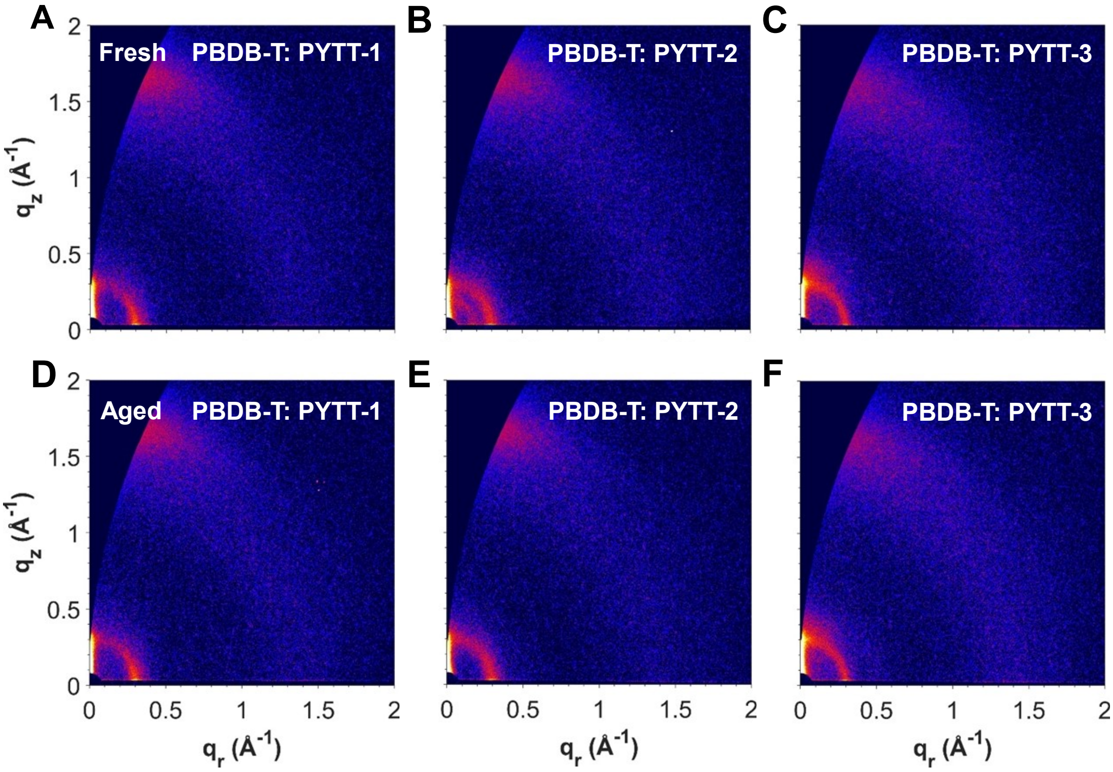

**Figure S13**. 2D GIWAXS patterns of fresh (Top row: A-C) and aged (Bottom row: D-F) blend films based on different acceptors (A, D) PYTT-1, (B, E) PYTT-2, and (C, F) PYTT-3 blended with PBDB-T.

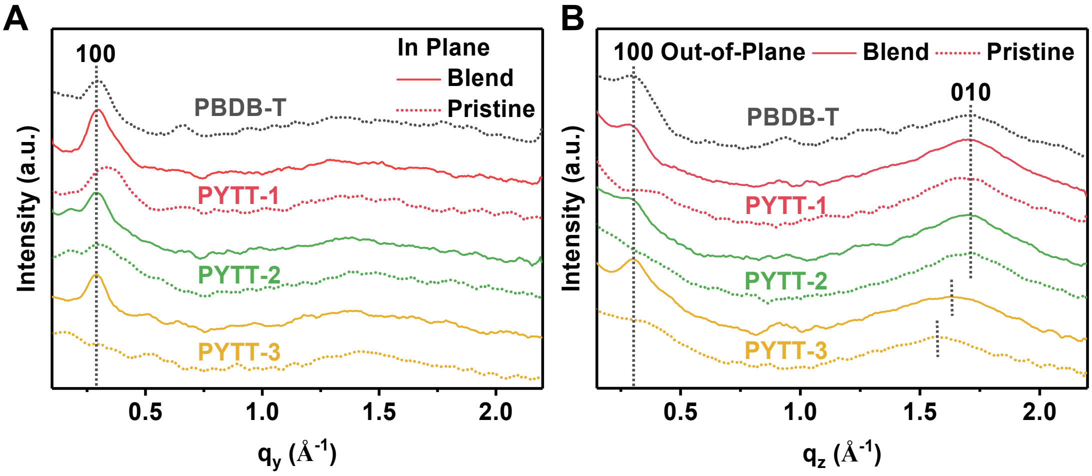

**Figure S14**. (A) In-plane (IP) direction and (B) out-of-plane (OOP) direction of grazing incidence wide-angle X-ray scattering (GIWAXS) line cuts for fresh pristine (short dash line) and blend films (solid line) based on different acceptors.

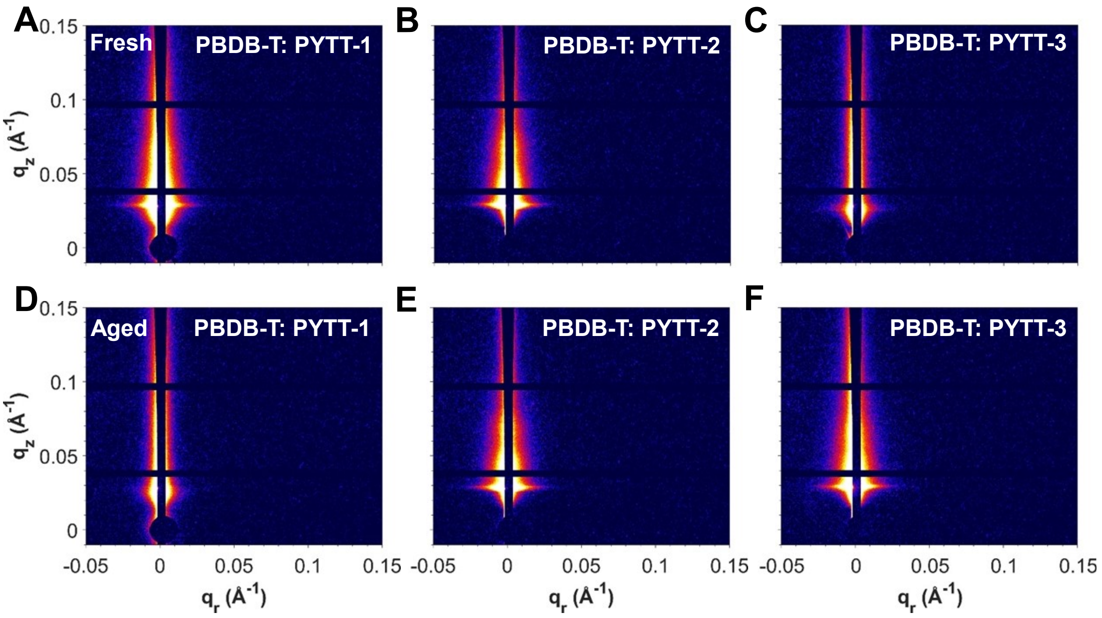

**Figure S15**. 2D GISAXS patterns of (Top row: A-C) fresh and (Bottom row: D-F) aged blend films based on different acceptors (A, D) PYTT-1, (B, E) PYTT-2, and (C, F) PYTT-3 blended with PBDB-T.

**Table S3**. The structure parameters determined from GISAXS profiles of fresh and aged films.

| Parameters | State | PBDB-T:PYTT-1 | PBDB-T:PYTT-2 | PBDB-T:PYTT-3 |
|---|---|---|---|---|
| Amorphous phase size (Å) | Fresh | 300 | 180 | 300 |
| | Aged | 440 | 180 | 220 |
| Rg (Å) | Fresh | 125.1 | 145.6 | 100.6 |
| | Aged | 82.6 | 152.5 | 153.4 |

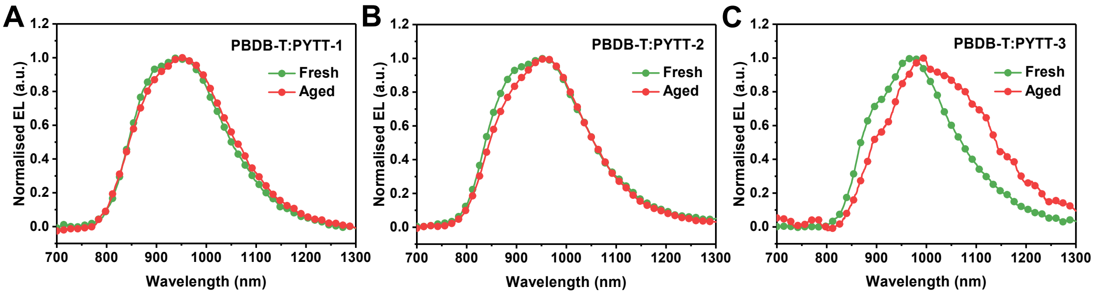

**Figure S16**. Electroluminescence (EL) spectra for fresh and aged devices based on different acceptors (A) PYTT-1, (B) PYTT-2, and (C) PYTT-3 blended with PBDB-T measured at an external constant current of 80 mA.

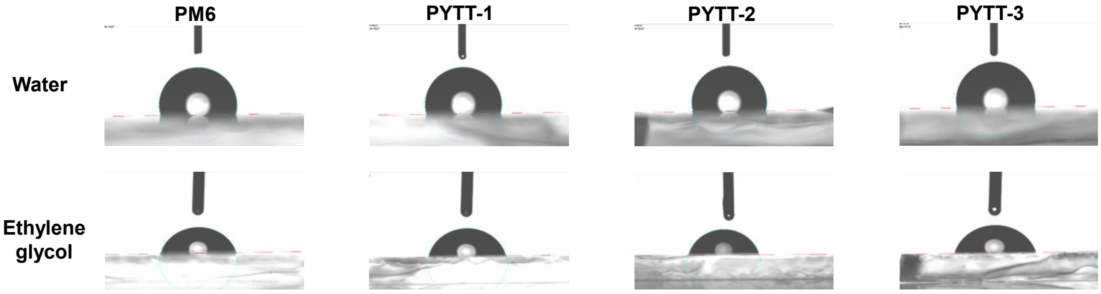

**Figure S17**. The contact angle of water, ethylene glycol on the top of PBDB-T, PYTT-1, PYTT-2 and PYTT-3 neat films.

**Table S4**. The summary of contact angle (θ), surface energy (γ) and Flory-Huggins interaction parameter (χ).

| Materials | $\theta_{water}$ [°] | $\theta_{ethylene\ glycol}$ [°] | γ [mN m$^{-1}$] | $^{a}\chi^{D\text{-}A}$ |
|---|---|---|---|---|
| PBDB-T | 106.0 | 75.7 | 37.14 | |
| PYTT-1 | 105.6 | 77.3 | 32.46 | 0.158 |
| PYTT-2 | 104.2 | 76.0 | 32.29 | 0.169 |
| PYTT-3 | 101.2 | 73.0 | 32.39 | 0.162 |

[a] The Flory–Huggins interaction parameter between the donor (D) and acceptor (A) is calculated according to the equation of $\chi^{D\text{-}A} = (\sqrt{\gamma_D} - \sqrt{\gamma_A})^2$.

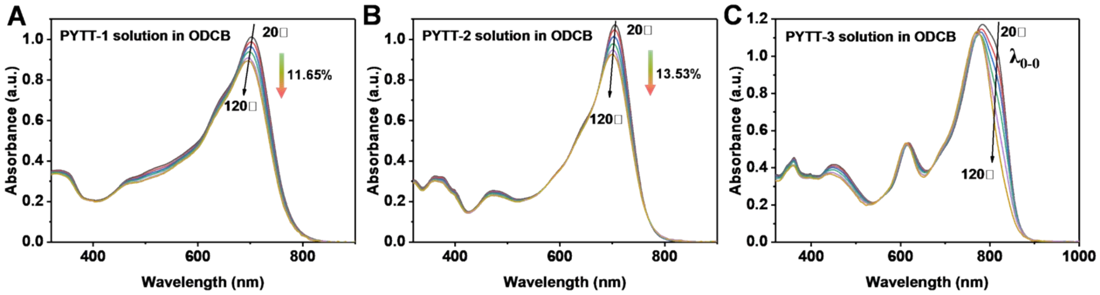

**Figure S18**. The temperature-dependent UV-vis spectra of (B) PYTT-1, (C) PYTT-2, (D) PYTT-3 in o-dichlorobenzene (ODCB) diluted solution with a concentration of 0.014mg/ml.

## References

(1) Wang, T.; Sun, R.; Wang, W.; Li, H.; Wu, Y.; Min, J. Highly Efficient and Stable All-Polymer Solar Cells Enabled by Near-Infrared Isomerized Polymer Acceptors. *Chem. Mater.* **2021**, *33*, 761–773.

(2) Vollbrecht, J.; Brus, V. V.; Ko, S.-J.; Lee, J.; Karki, A.; Cao, D. X.; Cho, K.; Bazan, G. C.; Nguyen, T.-Q. Quantifying the Nongeminate Recombination Dynamics in Nonfullerene Bulk Heterojunction Organic Solar Cells. *Adv. Energy Mater.* **2019**, *9*, 1901438.

(3) Brus, V. V.; Proctor, C. M.; Ran, N. A.; Nguyen, T.-Q. Capacitance Spectroscopy for Quantifying Recombination Losses in Nonfullerene Small-Molecule Bulk Heterojunction Solar Cells. *Adv. Energy Mater.* **2016**, *6*, 1502250.

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