## Supporting Information

## Highly Efficient and Highly Stable Terpolymer-based All-Polymer Solar Cells with Broad Complementary Absorption and Robust Morphology

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## Experimental

### Materials and Synthesis

All chemicals were purchased from Sigma-Aldrich and Acros Organics and used without further purification. The reagent-grade solvents used in this study were freshly dried using standard methods. Binary copolymers, Co-3MT and Co-TPD were synthesized using modified literature procedures.[1,2]

***Synthesis of poly[methyl acetate compound with 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-2-(thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene],*** **Co-3MT:** The polymer Co-3MT is a deep red solid ($M_n$ = 26.7 kDa, polydispersity index (PDI) = 2.52). Elemental Anal. calcd for $C_{40}H_{46}O_2S_5$: C, 66.81; H, 6.45; O, 4.45; S, 22.29. Found: C, 65.98; H, 6.24; S, 21.63.

***Synthesis of poly[1-(6-(5-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)thiophen-2-yl)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione],*** **Ter-**

**3MTTPD:** A dry Schlenk tube equipped with a screw cap was charged with (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (300 mg, 0.332 mmol), freshly recrystallized 1,3-dibromo-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (70.2 mg, 0.166 mmol), and methyl 2,5-dibromothiophene-3-carboxylate (49.7 mg, 0.166 mmol). Pd$_2$(dba)$_3$ (3.04 mg, 3.32 μmol) and P(o-tolyl)$_3$ (4.04 mg, 13.3 μmol) were added to the solution and the mixture was allowed to stir at 110 °C for 42 h under nitrogen atmosphere. The slightly viscous bluish-purple solution was cooled to room temperature and poured into 200 mL of methanol to obtain polymer precipitates. The resulting solids were subjected to Soxhlet extraction with acetone, hexane, and chloroform, successively. The polymer solution was further precipitated from methanol, and the solid was filtered to obtain Ter-3MTTPD as a reddish brown solid (172 mg, 98%) ($M_n$ = 32.2 kDa, PDI = 4.42). Elemental Anal. Calcd for C$_{88}$H$_{103}$NO$_4$S$_{10}$: C, 67.78; H, 6.66; N, 0.90; O, 4.10; S, 20.56. Found: C, 65.98; H, 6.15; N, 0.86; S, 20.07.

***Synthesis of poly[1-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione], Co-TPD:*** (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (200 mg, 0.221 mmol) and recrystallized 1,3-dibromo-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (94.6 mg, 0.221 mmol) were dissolved in 15 mL of anhydrous toluene degassed with nitrogen for 20 min. Pd$_2$(dba)$_3$ (4.05 mg, 4.42 μmol) and P(o-tolyl)$_3$ (5.38 mg, 17.7 μmol) were then added to the mixture, which was then heated to 110 °C and maintained at this temperature for 48 h under nitrogen atmosphere. The slightly viscous solution was cooled to room temperature, and the polymer was precipitated from methanol. The crude polymer was collected by filtration and then purified by Soxhlet extraction with acetone, hexane, and chloroform, successively. The polymer solution was subsequently precipitated from methanol and filtered, to obtain the binary copolymer, Co-TPD as a dark reddish brown solid (169 mg,

91%.) ($M_n$ = 13.7 kDa, PDI = 4.22). Elemental Anal. calcd for $C_{48}H_{59}NO_2S_5$: C, 68.45; H, 7.06; N, 1.66; O, 3.80; S, 19.03. Found: C, 67.85; H, 6.74; N, 1.52; S, 18.79.

## *Instrumentation*

The number average molecular weights ($M_n$s) and PDIs of the binary and ternary copolymers were estimated by gel permeation chromatography (GPC; Agilent GPC 1200 series) at 80 °C with *o*-dichlorobenzene as the eluent and polystyrene as the standard. The absorption spectra of the copolymers and terpolymer in chloroform (CF) solutions and thin films were recorded using a UV−vis absorption spectrometer (Agilent 8453, photodiode array, $\lambda$ = 190−1100 nm). Steady-state photoluminescence (PL) spectra of the polymers were obtained in solution and film states using a spectrophotometer (Hitachi F-7000). The electrochemical properties were characterized by cyclic voltammetry (CV, eDAQ EA161), using an electrolyte solution prepared by dissolving tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$) in acetonitrile. A Pt wire and Ag/AgCl system were used as the counter and reference electrodes, respectively. The copolymers and terpolymer were dissolved in the electrolyte solution for CV measurements.

Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted at the 9 Å beamline (energy = 11.05 keV, pixel size = 79.59 μm, $\lambda$ = 1.12199 Å, $2\theta$ = 0−20°) of the Pohang Accelerator Laboratory. Films were prepared by spin-coating the polymer solutions onto a $SiO_2$ wafer. The surface morphologies of films were explored using an atomic force microscope (XE-100, Advanced Scanning Probe Microscope, PSIA) with a silicon cantilever. Transmission electron microscopy (TEM) was employed to observe the internal morphology of thin films (Tecnai G2F30 transmission electron microscope, FEI Inc.; accelerating voltage = 300 kV). Samples for TEM observations were prepared by coating the polymer blend solution on a carbon-coated copper grid.

## *Measurement of time-resolved photoluminescence (TRPL)*

Time-resolved PL spectroscopy and imaging were performed using an inverted-type scanning confocal microscope (MicroTime-200, Picoquant, Germany) with a 100× oil-immersion objective. A single-mode pulsed diode laser (LDH-P-C-470, Picoquant, Germany) with a 20 MHz repetition rate, ~30 ps pulse width, and 5 μW average power was used as the excitation source. A dichroic mirror (490 DCXR, AHF), a long-pass filter (HQ500lp, AHF), a 75 μm pinhole, additional band-pass filters (600–700 nm), and a single photon avalanche diode (PDM series, MPD) were used to collect the emissions from the samples. Time-correlated single-photon counting (TCSPC) technique was employed to count the emission photons. TRPL images consisted of 200 × 200 pixels recorded using the time-tagged time-resolved (TTTR) data acquisition method. Exponential fittings for the obtained fluorescence decays, which were extracted from the TRPL images, were performed using Symphotime-64 software (Ver. 2.2) using a biexponential decay model, $I(t) = \sum A_i \exp(-t/\tau_i)$, where, $I(t)$ is the time-dependent PL intensity, $A$ is the amplitude, $\tau$ is the PL lifetime, and $i$ is 2 in this study. The average PL lifetime ($\tau_{ave}$) is deduced by the following equation; $\tau_{ave} = \sum_i A_i\tau_i / \sum_i A_i$ .


## *Fabrication and stability of all-polymer solar cells (all-PSCs)*

Inverted type all-PSCs in this study were fabricated using the literature method.[1,3] Each of the polymer:NDI-Se blends was obtained by spin-coating the respective chlorobenzene (CB) solution (1.5 wt%) with polymer:NDI-Se = 2:1 wt. ratio. The blend solutions were stirred overnight at 60 °C and spin-coat onto the ITO/ZnO substrate at 3000 rpm for 40 s. Finally, $MoO_3$ and Ag were deposited on the photoactive layer by thermal evaporation. The current density−voltage ($J$−$V$) characteristics were measured using a Keithley 2400 source meter under

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AM 1.5 G illumination at 100 mW cm$^{-2}$ (Oriel, 1000 W). The device stability was investigated without encapsulation and by storing under ambient conditions up to 1000 h.[4] The intensity of the incident light was measured by a calibrated broadband optical power meter (Spectra Physics, model 404). External quantum efficiency (EQE) spectra were recorded by a K3100 EQX instrument with a K240 XE300 lamp source.

## *Measurement of charge mobility through space-charge-limited current (SCLC) method*

Hole-only devices, with the structure of ITO/PEDOT:PSS/active layer/Au, and electron-only devices with the configuration of ITO/ZnO/active layer/LiF/Al, were fabricated[1]. Each active layer was fabricated under conditions identical to those used for fabricating the corresponding all-PSCs. The hole and electron carrier mobilities were determined using the modified Mott-Gurney equation, $J = (9/8)\varepsilon_0\varepsilon_r\mu(V^2/L^3)$, where $J$ is the current density, $\mu$ is the mobility, and $V$ is the applied voltage, and the device thickness, $L$, is defined. Moreover, $\varepsilon_0$ is the vacuum permittivity and $\varepsilon_r$ is the relative permittivity.[5]
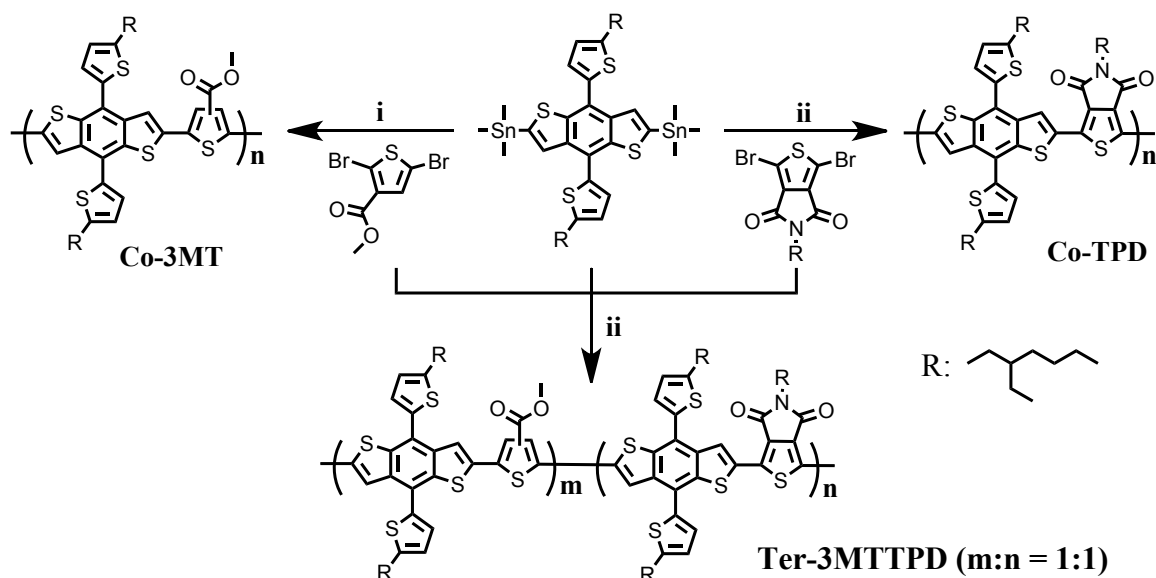
**Scheme S1.** Synthetic procedure for binary copolymers and the terpolymer: i) Pd$_2$(dba)$_3$, P(*o*-tolyl)$_3$, toluene/dimethyl formamide (10:1, v/v), 100 °C, ii) Pd$_2$(dba)$_3$, P(*o*-tolyl)$_3$, toluene, 110 °C.
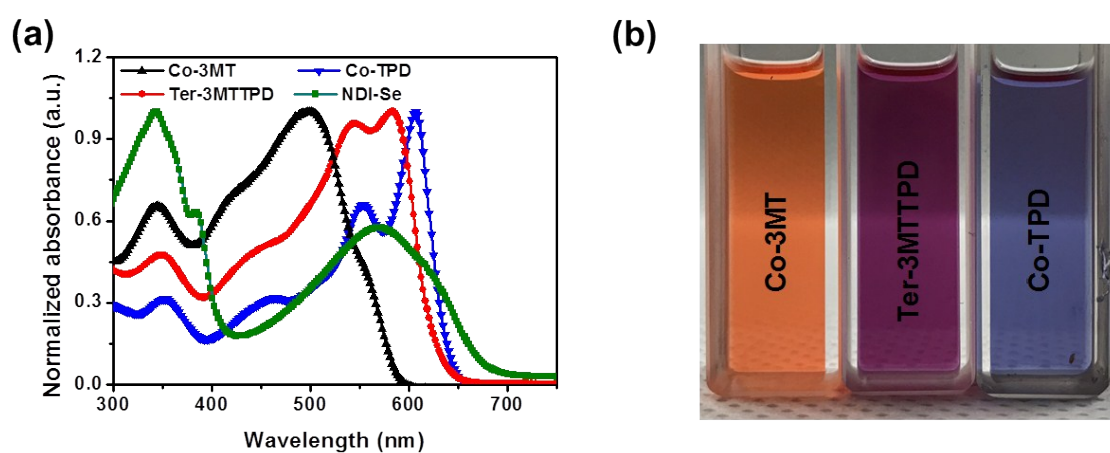


**Fig. S1.** (a) Normalized optical absorption spectra of solutions of Co-3MT, Ter-3MTTPD, Co-TPD, and NDI-Se in chloroform and (b) photographs of the three polymer solutions at room temperature.
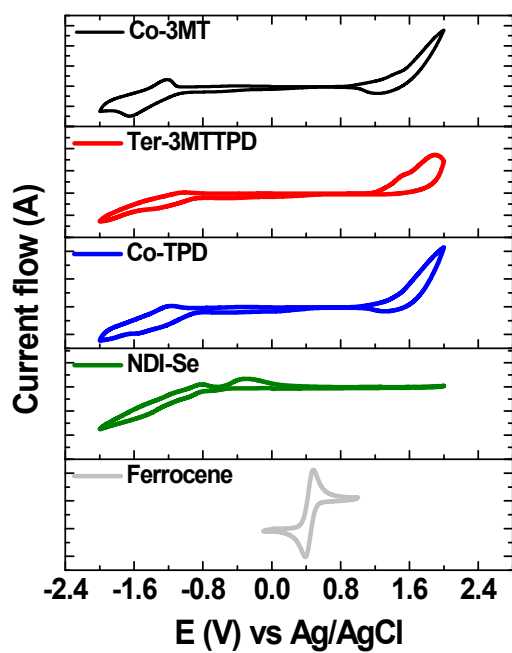
**Fig. S2.** (a) Cyclic voltammograms of the films of Co-3MT, Ter-3MTTPD, Co-TPD, and NDI-Se.
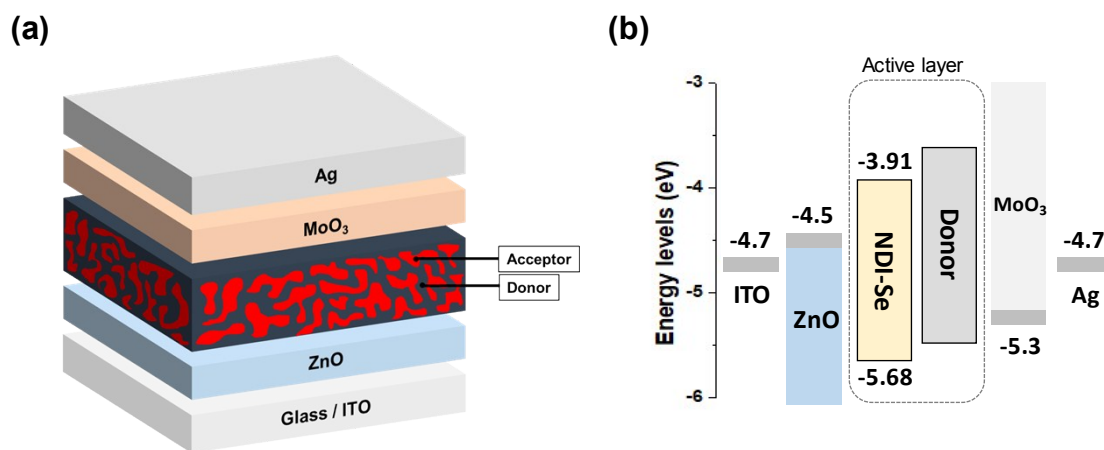


**Fig. S3.** (a) Device configuration of all-PSCs and (b) Energy level diagram of inverted type PSC.

**Table S1.** Photovoltaic properties of Co-3MT, Ter-3MTTPD, and Co-TPD-based all-polymer solar cells with NDI-Se.

| Polymer | Wt. ratio (D:A) | Conc. (wt %) | Solvent | Additive (vol. %) | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | $\eta$ (%) |
|---|---|---|---|---|---|---|---|---|
| Ter-3MTTPD | 1 : 2 | 1.5 | CB | - | 8.94 | 1.00 | 44.9 | 4.02 |
| | 1 : 1 | 1.5 | CB | - | 10.20 | 1.01 | 56.3 | 5.79 |
| | 2 : 1 | 1.5 | CB | - | 10.17 | 1.00 | 58.5 | 5.98 |
| | 2 : 1 | 1.0 | CF | | 10.14 | 1.01 | 58.3 | 5.95 |
| | 2 : 1 | 1.5 | CB | 0.5 DIO | 10.39 | 1.00 | 53.7 | 5.60 |
| | 2 : 1 | 1.5 | CB | 1.0 DIO | 11.42 | 1.01 | 63.1 | 7.28 |
| | 2 : 1 | 1.5 | CB | 2.0 DIO | 9.23 | 1.02 | 57.8 | 5.63 |
| | 2 : 1 | 1.5 | CB | 0.25 DPE | 10.27 | 0.99 | 56.1 | 5.71 |
| | 2 : 1 | 1.5 | CB | 1.0 DPE | 10.74 | 1.01 | 64.5 | 6.99 |
| | 2 : 1 | 1.5 | CB | 2.0 DPE | 11.47 | 1.01 | 66.2 | 7.66 |
| | 2 : 1 | 1.5 | CB | 3.0 DPE | 10.30 | 1.02 | 63.5 | 6.67 |
| Co-3MT | 2 : 1 | 1.5 | CB | - | 2.87 | 0.93 | 54.3 | 1.45 |
| | 2 : 1 | 1.5 | CB | 2.0 DPE | 3.40 | 0.93 | 54.7 | 1.73 |
| Co-TPD | 2 : 1 | 1.5 | CB | | 5.06 | 0.98 | 33.5 | 1.66 |
| | 2 : 1 | 1.5 | CB | 2.0 DPE | 4.62 | 1.08 | 50.3 | 2.51 |

* DIO, 1,8-diiodooctane; DPE, diphenyl ether
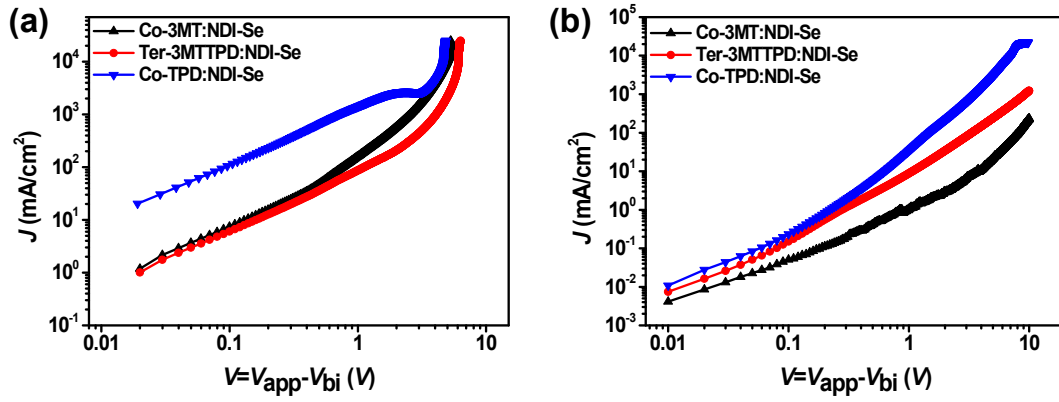
**Fig. S4.** Space-charge-limited *J–V* characteristics of the blend films obtained under dark conditions for (a) hole only devices and (b) electron only devices.
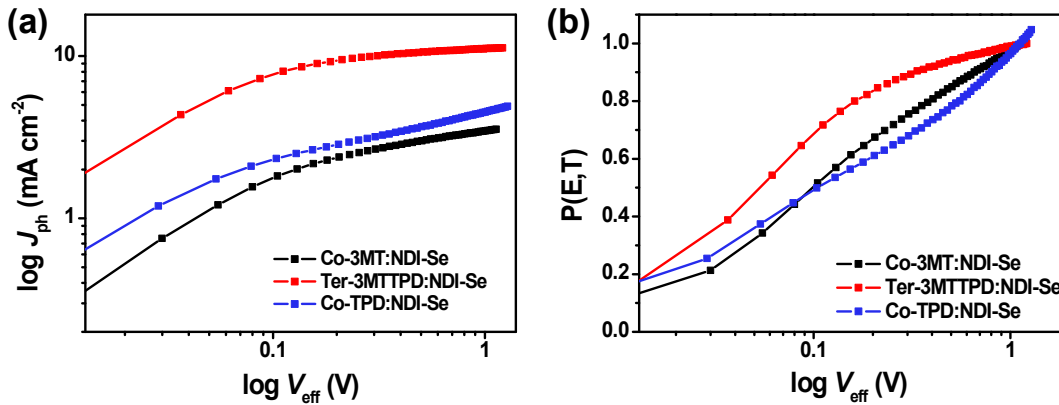


**Fig. S5.** Photocurrent density ($J_{ph}$) and exciton dissociation probability [$P(E,T)$] versus effective bias ($V_{eff}$).
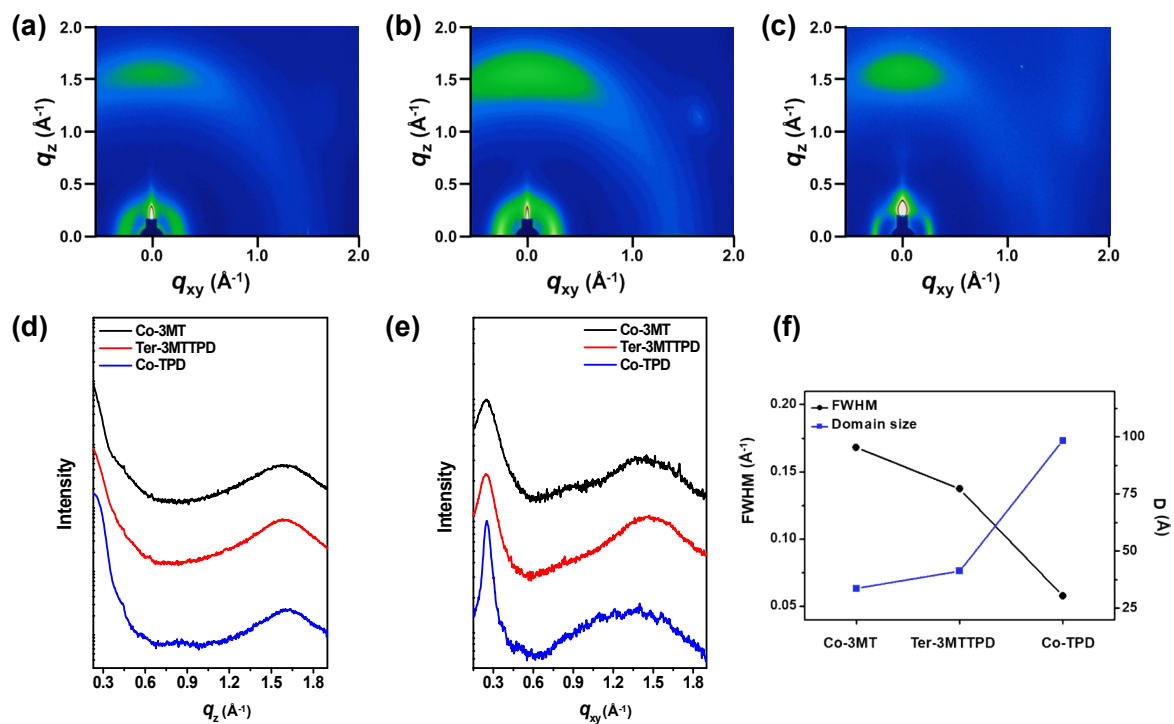
**Fig. S6.** (a–c) 2D grazing incidence wide angle X-ray scattering (GIWAXS) patterns of neat films of (a) Co-3MT, (b) Ter-3MTTPD, and (c) Co-TPD. (d) Out-of-plane and (e) in-plane profiles of the neat films and (f) full width at half maximum (FWHM) and domain size calculated from the (100) diffraction peak in the in-plane profiles of the Co-3MT, Ter-3MTTPD, and Co-TPD neat films.
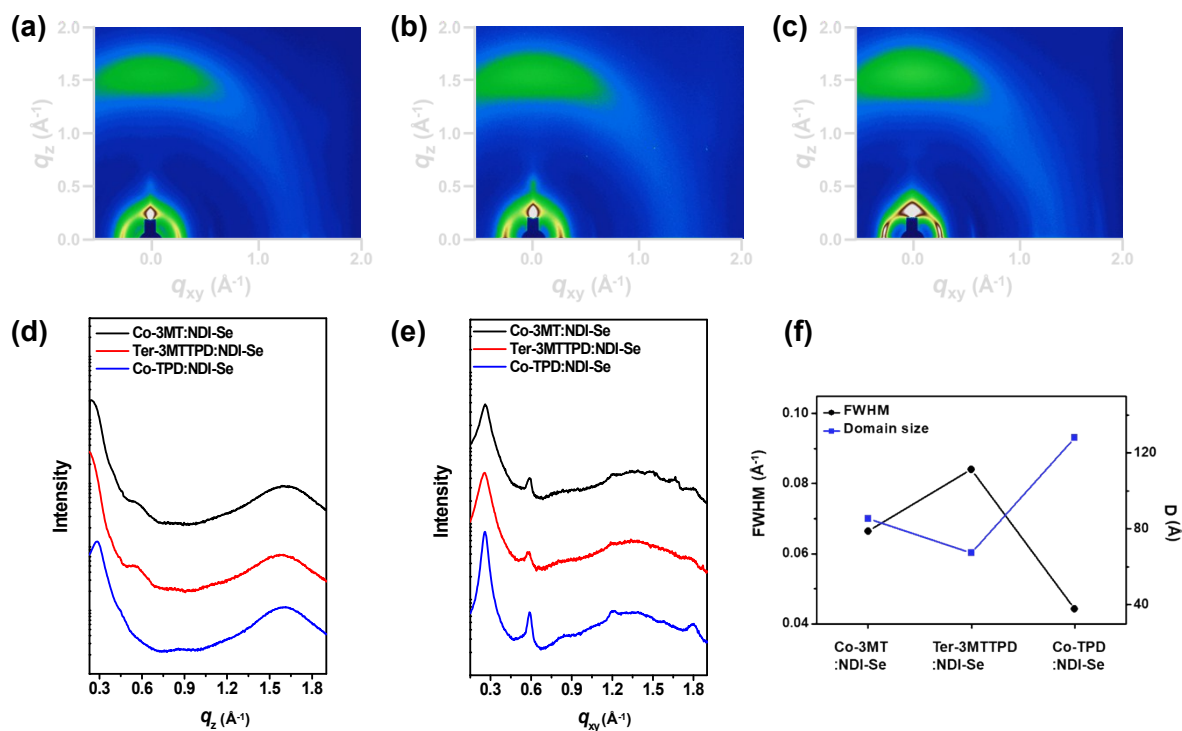
**Fig. S7.** (a–c) GIWAXS patterns of blend films of three polymers with 2 vol.% DPE: (a) Co-3MT:NDI-Se, (b) Ter-3MTTPD:NDI-Se, and (c) Co-TPD:NDI-Se. (d) Out-of-plane and (e) in-plane profiles of the blend films. (f) Full width at half maximum (FWHM) and domain size calculated from the (100) diffraction peak in the in-plane profiles of the blend films.

GIWAXS can be used to study the crystallinity of a polymer and the arrangement of polymer chains or crystallites on a substrate. The GIWAXS patterns for as-cast films of three polymers and the blend films with polymer and NDI-Se are shown in **Fig. S6** and **S7**. All the neat films (**Fig. S6**) show relatively intense (100) X-ray reflection at $q_{xy} \approx 0.24$–$0.25$ Å$^{-1}$ in the in-plane GIWAXS pattern and (010) reflection at $q_z \approx 1.6$ Å$^{-1}$ in the out of plane GIWAXS pattern, indicating that a face-on orientation is predominant. As shown in **Fig. S7**, blend films also showed strong face-on orientation favorable for the photovoltaic application with the (010) π-π stacking peak and (100) diffraction peak in the in-plane direction. In **Table S2**, the FWHM of the (100) diffraction peaks in the in-plane diffraction and crystal coherence length (crystallite size, $D$) estimated using the Scherrer equation are summarized.[6] Overall, blend films of the two binary copolymers showed much larger crystal coherence length compared to Ter-3MTTPD. The Ter-3MTTPD blend film had the smallest crystal coherence length of 67.4 Å, which could

explain the optimal morphology of the terpolymer with nanophase segregation.

**Table S2.** Peak assignments for the (100) in-plane GIWAXS profiles of the neat polymer and blend films.

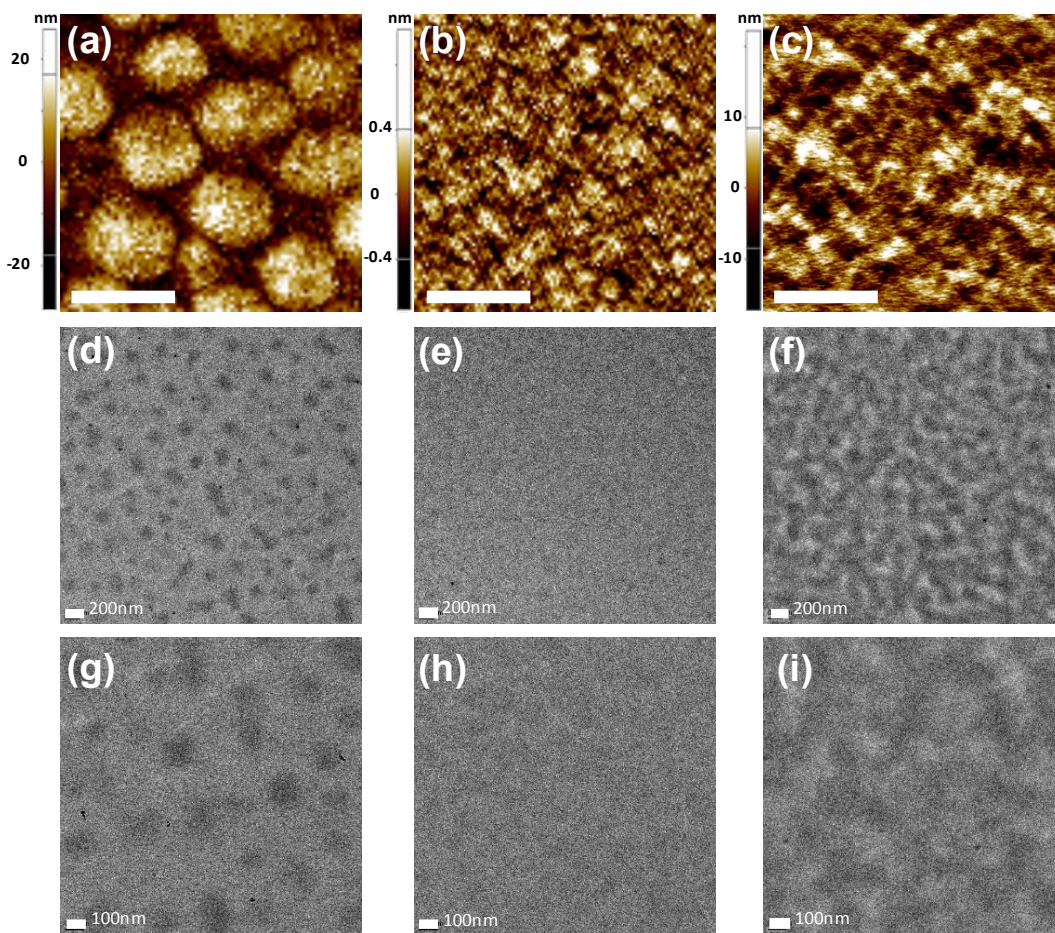|  |  | $q$ (Å$^{-1}$) | $d$-spacing (Å) | FWHM (Å$^{-1}$) | $D$ (Å) |
|---|---|---|---|---|---|
| **Neat films** | Co-3MT | 0.24 | 25.88 | 0.1681 | 33.64 |
|  | Ter-3MTTPD | 0.24 | 26.12 | 0.1372 | 41.23 |
|  | Co-TPD | 0.25 | 24.97 | 0.0575 | 98.30 |
| **Blend films with NDI-Se** | Co-3MT | 0.26 | 24.12 | 0.0664 | 85.40 |
|  | Ter-3MTTPD | 0.26 | 24.54 | 0.0841 | 67.40 |
|  | Co-TPD | 0.26 | 24.12 | 0.0443 | 128.1 |

**Fig. S8.** AFM height images (1.5 μm × 1.5 μm, scale bar: 500 nm) of the optimized blend films (2:1 wt. ratio) prepared in chlorobenzene with 2 vol.% DPE. (a) Co-3MT:NDI-Se, (b) Ter-3MTTPD:NDI-Se, and (c) Co-TPD:NDI-Se. (a) Rq= 7.76 nm, (b) Rq= 0.25 nm, (c) Rq= 4.31 nm. TEM images (scale bar on the left side of the image) of the optimized blend film. (d,g) Co-3MT:NDI-Se, (e,h) Ter-3MTTPD:NDI-Se, and (f,i) Co-TPD:NDI-Se.
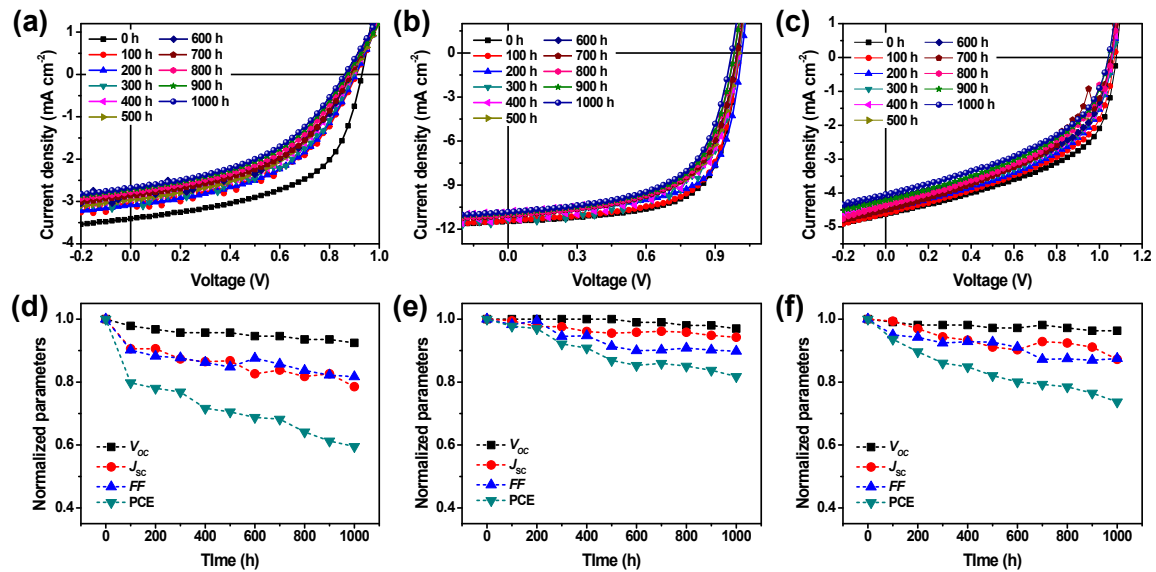
**Fig. S9.** Evaluation of the performance stability of an all-PSC under ambient conditions up to 1000 h of storage. Variation of $J$–$V$ characteristics of all-PSCs based on each blend film with 2 vol.% DPE: (a,d) Co-3MT:NDI-Se, (b,e) Ter-3MTTPD:NDI-Se, and (c,f) Co-TPD:NDI-Se blend films. The average photovoltaic parameters were obtained based on data from three samples.
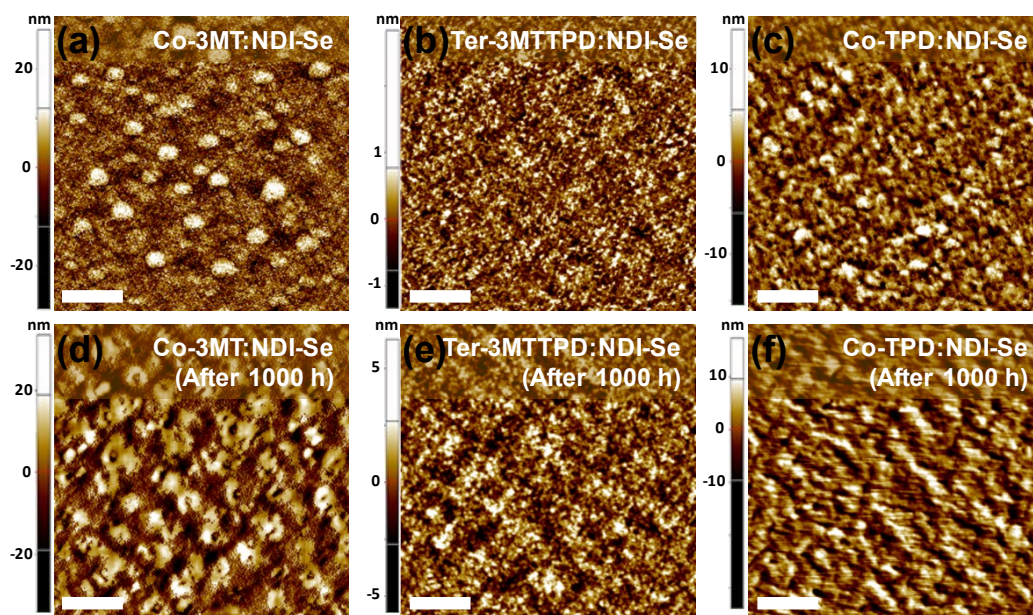


**Fig. S10.** AFM height images (5 $\mu$m × 5 $\mu$m, scale bar: 1 μm) of the active layer in the all-PSC device: (a,d) Co-3MT:NDI-Se with 2 vol.% DPE, (b,e) Ter-3MTTPD:NDI-Se with 2 vol.% DPE, and (c,f) Co-TPD:NDI-Se with 2 vol.% DPE. (a,b,c) are for pristine films and (d,e,f) are for films stored for 1000 h under ambient conditions.

## Reference

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