Supporting Information

Ester-Functionalized, Wide-Bandgap Derivatives of PM7 for Simultaneous Enhancement of Photovoltaic Performance and Mechanical Robustness of All-Polymer Solar Cells

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Methods

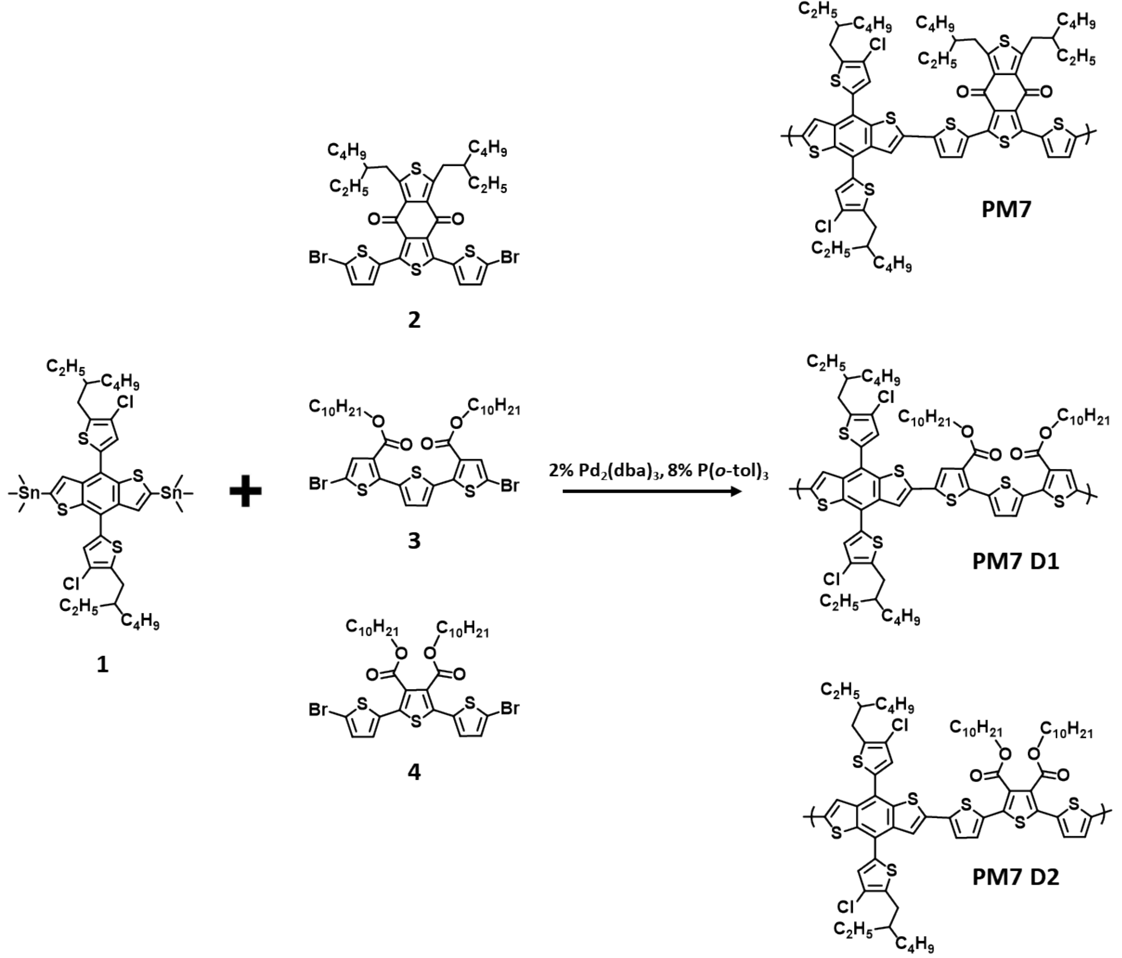
Characterizations

All reactions were carried out under argon gas. ^{1}H NMR for the all donor polymers was acquired by a Bruker 400 MHz instrument using 1,1,2,2-tetrachloroethane ($C_2D_2Cl_4$) or 1,2-dichlorobenzene ($C_6D_4Cl_2$) at 100 °C; the residual $C_2H_2Cl_4$ (^{1}H: δ= 6.0 ppm), or $C_6H_4Cl_2$ (^{1}H: δ= 7.4 ppm) peaks were used as references for the chemical shifts of the reported polymers in this study. Gel permeation chromatography (GPC) experiment was conducted using a Tosoh EcoSEC high-temperature GPC instrument with RI detector to determine the number average molecular weight (M_n) and the dispersity ($Đ$) for the all donor and acceptor polymers. GPC experiments were run using 1, 2, 4-trichlorobenzene (TCB) as eluent at 140 °C with a flow rate of 1 mL min^{-1} on two 7.8 mm × 30 cm, 13 μm TSK-Gel GMH$_{HR}$-H(S) HT2 columns in series. The instrument was calibrated using polystyrene standards (1,390-1,214 kg mol^{-1}) and the data were analyzed using the 8321GPC-WS analysis software. The GPC samples were prepared by dissolving the polymers in TCB (1 mg mL^{-1}) and stirred at 110 °C for at least 3 hours before filtering through a 0.45 mm PTFE filter. Elemental analyses were performed by Atlantic Microlab Inc. The UV-vis absorption spectra of solution and film states were measured from UV-1800 spectrophotometer (Shimadzu Scientific Instruments) at room temperature. Polymer films on glass substrates were prepared by spin-coating the solution (10 mg mL^{-1} in chlorobenzene) at 3000 rpm for 40 s with a ramp time of 0.1 s. Differential pulsed voltammetry (DPV) was performed using a 2 mV step size, 80 ms step time, and 50 mV pulse amplitude. The DPV experiments were performed in argon-filled glove box using a standard three-electrode cell including a 0.07 cm^2 glassy carbon button working electrode, an Ag/Ag$^+$ (0.01 M $AgNO_3$) reference electrode, and a platinum flag counter electrode. Polymer films were prepared by drop-casting 1 mg mL^{-1} chloroform solution onto the working electrode. The DPV experiments were conducted using dry acetonitrile with a $TBAPF_6$ supporting electrolyte at a concentration of 0.5 M. Fc/Fc$^+$ (−5.12 V vs vacuum) was used as an internal standard calibration against the Ag/Ag$^+$ reference electrode ($E_{1/2}$ = 85 mV). Grazing incidence X-ray scattering (GI-WAXS) was performed at the beamline 3C in the Pohang Accelerator Laboratory (South Korea). The pristine thin films were prepared by spin-coating the polymer solution (10 mg mL^{-1} in chlorobenzene) at 3000 rpm for 40 s with a ramp time of 0.1 s on bare Si substrates and the blend films were prepared at the same condition as described in the device fabrication section. The wavelength of X-ray was 1.2301 Å and the incidence angle (about 0.12^o) was chosen for complete penetration of X-ray into the polymer film. Resonant soft X-ray scattering (RSoXS) experiments were conducted at BL 11.0.1.2 in the Advanced Light Source (USA). Density functional theory (DFT) calculation was performed using B3LYP/6-31* basis set with the Spartan 14 package and all alkyl chains on the polymers were replaced with methyl group to simplify the calculation.

Materials

3-Thiophenecarboxylic acid was purchased from TCI America, thiophene-3,4-dicarboxylic acid was purchased from Santa Cruz Biotechnology and 2-(tributylstannyl)thiophene was purchased from Sigma Aldrich. 4,9-Dibromo-2,7-bis(hexyldecyl)benzo[*lmn*][3,8]-phenanthroline-1,3,6,8-tetraone and (4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (monomer 1) was purchased from SunaTech. Poly{[*N*,*N*'bis(2-hexyldecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-2,5-selenophene} (P(NDI2HD-Se)) and 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-butyloctyl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione (monomer 2) were synthesized according to the published procedures.[1, 2]

Synthesis of polymers



General polymerization procedure for all PM7, PM7 D1, and PM7 D2. A dry 50 mL round bottom flask was equipped with a magnetic stir bar, designated brominated monomer, and monomer 1. Didecyl 5,5''-dibromo-[2,2':5',2''-terthiophene]-3,3''-dicarboxylate (monomer 3) and didecyl 5,5''-dibromo-[2,2':5',2''-terthiophene]-3',4'-dicarboxylate (monomer 4) were synthesized as described in our previous literature.[3] The flask was transferred into a glove box where Pd$_2$(dba)$_3$•CHCl$_3$ and P(*o*-tol)$_3$ were added. After the vessel was equipped with a condenser, sealed and removed from the glove box, a constant flow of argon was immediately applied to the flask. After 3 mL of dry and recently argon purged chlorobenzene was added to the reaction vessel through the condenser, the solution was heated to 145 °C and allowed to react for 24 hours under argon condition. The solution was then cooled to 90 °C and exposed to air to add an excess amount of Pd scavenger diethylammonium diethyldithiocarbamate and

10 mL of additional chlorobenzene. The mixture was stirred for 1 hour before it was precipitated into 250 mL of methanol. The impure polymer was filtered through a nylon extraction thimble and subjected to successive Soxhlet extractions with methanol, acetone, hexanes, dichloromethane, and finally chloroform if needed. The Soxhlet solution with the desired product was concentrated under reduced pressure and precipitated into methanol. Finally, the pure polymer was collected *via* vacuum filtration and dried under vacuum for 24 hours.

PM7: Monomer 1 (200 mg, 0.205 mmol), monomer 2 (157 mg, 0.205 mmol), $Pd_2(dba)_3$•$CHCl_3$ (5 mg, 0.0048 mmol), P(*o*-tol)$_3$ (6 mg, 0.0197 mmol) and 3 mL of chlorobenzene were used. The polymer was collected in the chloroform Soxhlet fraction as a dark solid (240 mg, 93%). M_n: 50.5 kg mol^{-1}, M_w: 116 kg mol^{-1}, $Đ$: 2.3 (GPC in 1, 2, 4-trichlorobenzene vs polystyrene). ^{1}H NMR (400 MHz, $C_6D_4Cl_2$, 110 °C): δ (ppm) 7.99 (bs, 4H), 7.65 (bs, 4H), 3.62 (m, 4H), 3.17 (bs, 4H), 2.12 (bs, 4H), 1.85-1.50 (m, 32H), 1.35-1.07 (m, 24H). Anal. calcd. for $C_{68}H_{76}Cl_2O_2S_8$: C (65.20%), H (6.12%), S (20.47%); Found: C (65.14%), H (6.08%), S (20.50%).

PM7 D1: Monomer 1 (200 mg, 0.205 mmol), monomer 3 (159 mg, 0.205 mmol), $Pd_2(dba)_3$•$CHCl_3$ (5 mg, 0.0048 mmol), P(*o*-tol)$_3$ (6 mg, 0.0197 mmol) and 3 mL of chlorobenzene were used. The polymer was collected in the chloroform Soxhlet fraction as a dark solid (235 mg, 91%). M_n: 39.6 kg mol^{-1}, M_w: 107 kg mol^{-1}, $Đ$: 2.70 (GPC in 1, 2, 4-trichlorobenzene vs polystyrene). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 100 °C): δ (ppm) 7.70 (m, 4H), 7.54 (s, 2H), 7.35 (s, 2H), 4.36 (m, 4H), 2.97 (bs, 4H), 1.91-1.76 (m, 6H), 1.62-1.28 (m, 44H), 1.11-0.89 (m, 18H). Anal. calcd. for $C_{68}H_{84}Cl_2O_4S_7$: C (64.78%), H (6.72%), S (17.80%); Found: C (64.67%), H (6.65%), S (17.60%).

PM7 D2: Monomer 1 (232 mg, 0.238 mmol), monomer 4 (185 mg, 0.238 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (5 mg, 0.0048 mmol), P(*o*-tol)$_3$ (6 mg, 0.0197 mmol) and 3 mL of chlorobenzene were used. The polymer was collected in the chloroform Soxhlet fraction as a dark green solid (235 mg, 91%). M_n: 45.8 kg mol^{-1}, M_w: 94.8 kg mol^{-1}, $Đ$: 2.07 (GPC in 1, 2, 4-trichlorobenzene vs polystyrene). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 100 °C): δ (ppm) 7.70 (m, 2H), 7.34 (m, 6H), 4.32 (m, 4H), 2.96 (m, 4H), 1.87 (m, 2H), 1.74 (m, 4H), 1.62-1.25 (m, 44H), 1.10-0.88 (m, 18H). Anal. calcd. for $C_{68}H_{84}Cl_2O_4S_7$: C (64.78%), H (6.72%), S (17.80%); Found: C (64.87%), H (6.58%), S (17.74%).

Supplementary Figures and Tables

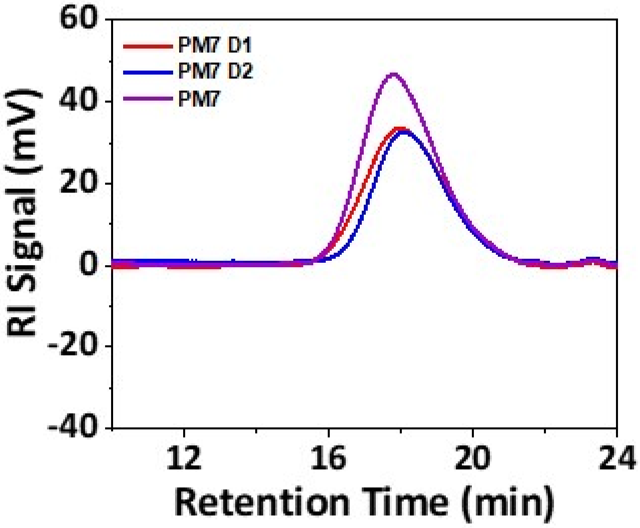


Fig. S1 High temperature (140 °C) GPC traces in 1,2,4-trichlorobenzene.

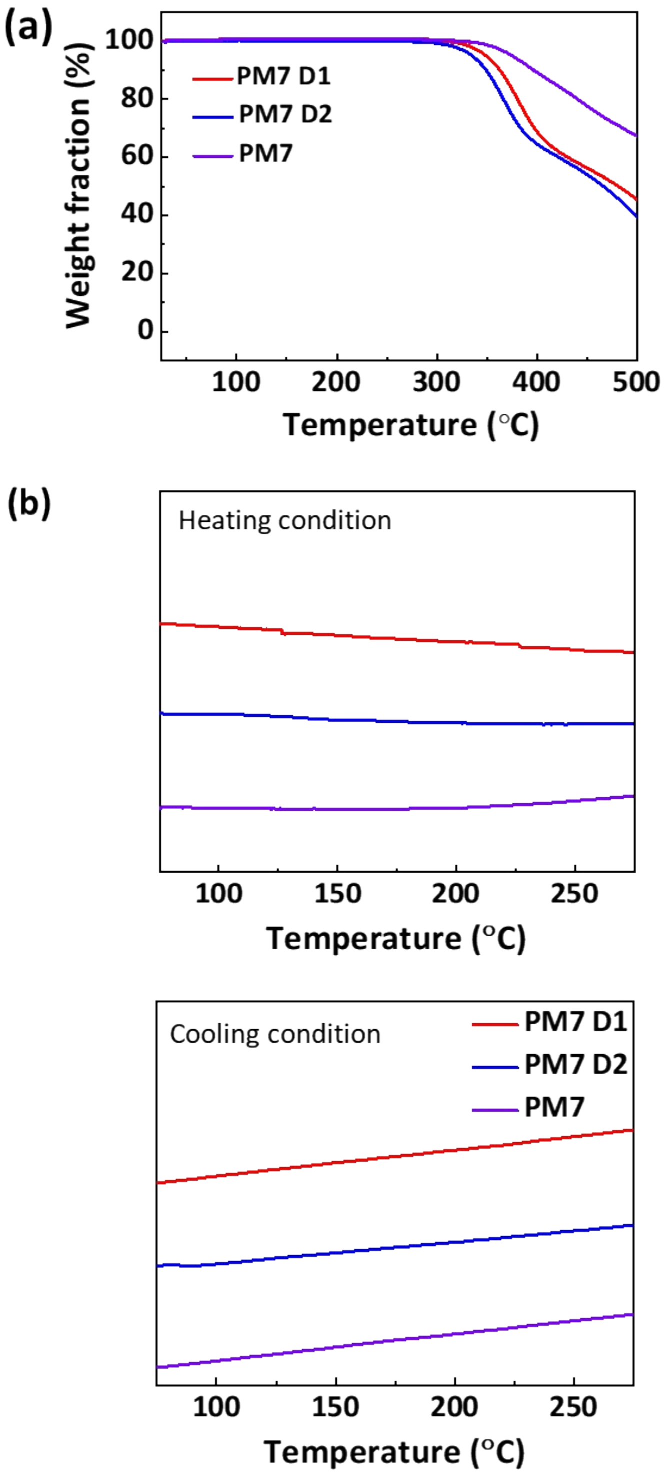


Fig. S2 (a) TGA curves and (b) second cycle DSC curves of PM7 D1, PM7 D2, and PM7.

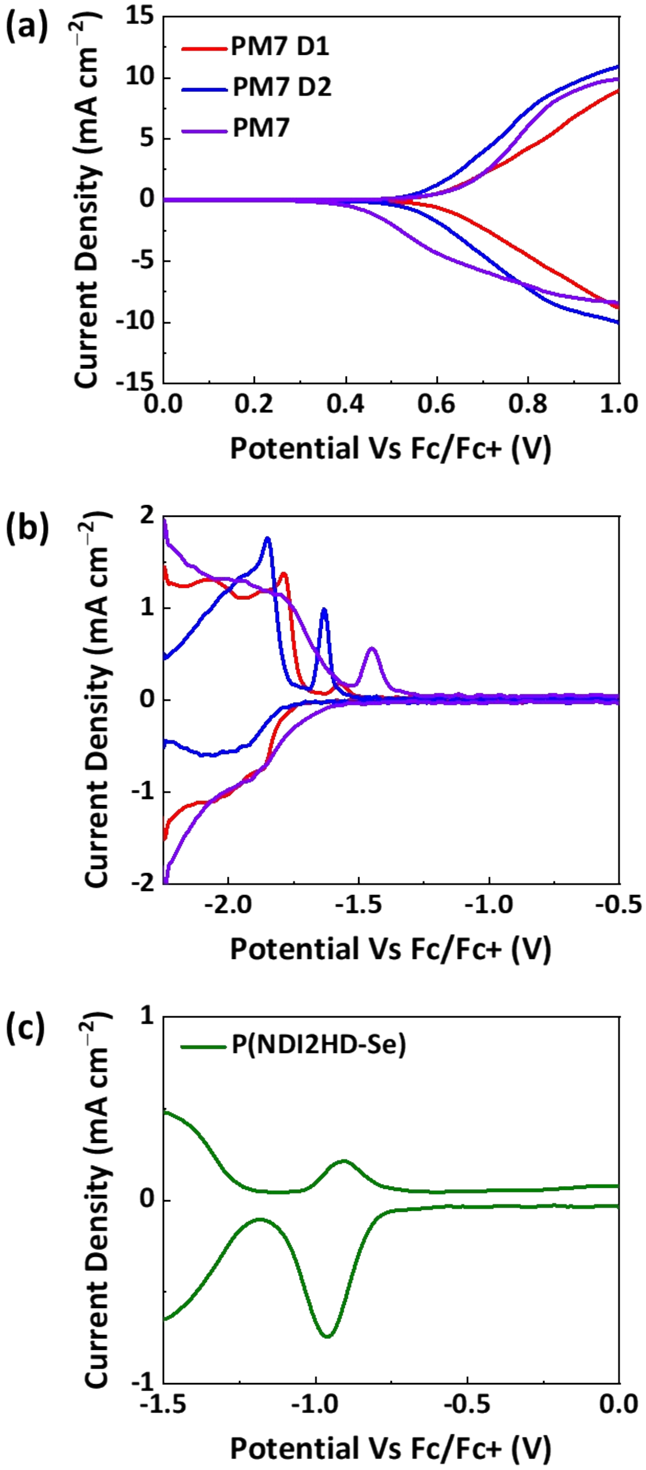


Fig. S3 Differential pulsed voltammetry (a) oxidation and (b) reduction curves for PM7 D1, PM7 D2, and PM7 and (c) reduction curve for P(NDI2HD-Se) versus Fc/Fc^{+}.[3]

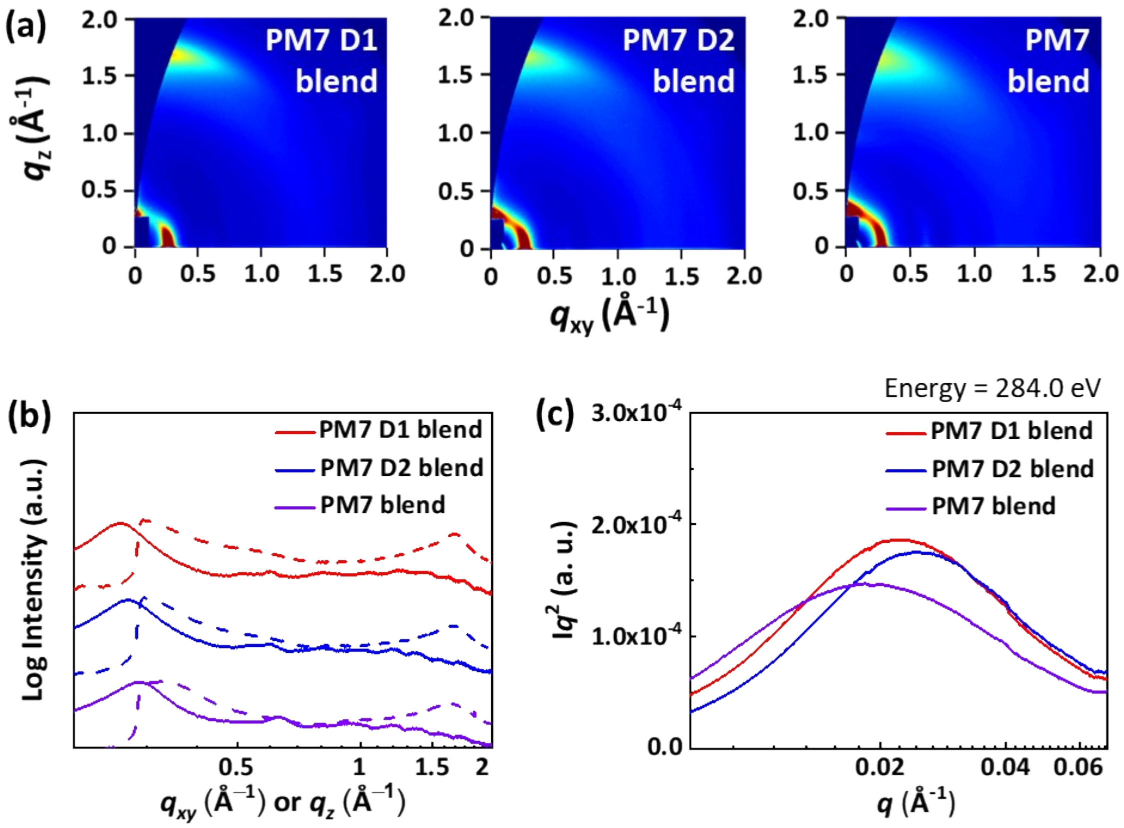


Fig. S4 (a) 2D GI-WAXS patterns, (b) in-plane (solid lines) and out-of-plane (dashed lines) line cut profiles of GI-WAXS, and (c) RSoXS profiles for blend films.

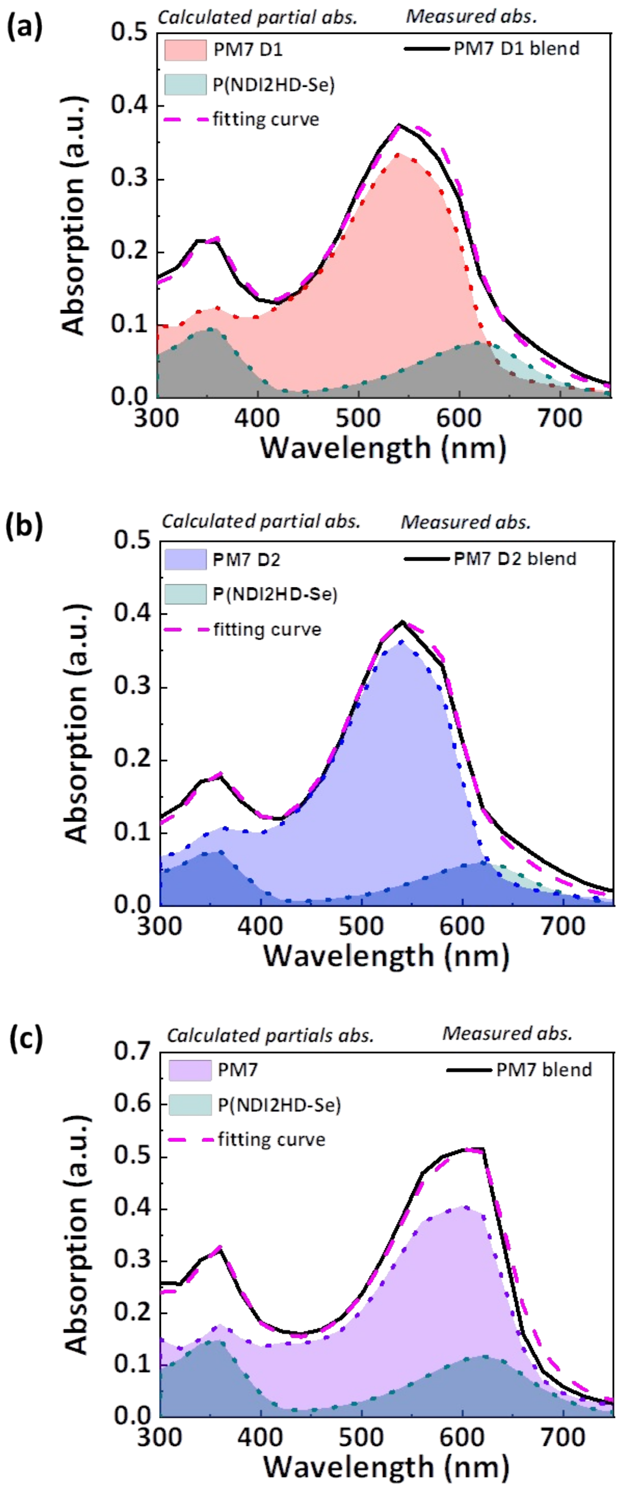


Fig. S5 The absorbance of the blend film and absorbance contribution of each component for (a) PM7 D1 (b) PM7 D2 and (c) PM7 blend films.

Table S1 Absorbance contribution of donor and acceptor to the total absorbance of PM7 D1, PM7 D2, and PM7 blend films.

Active layer	Donor	Acceptor
PM7 D1 blend	0.77	0.23
PM7 D2 blend	0.79	0.21
PM7 blend	0.73	0.27

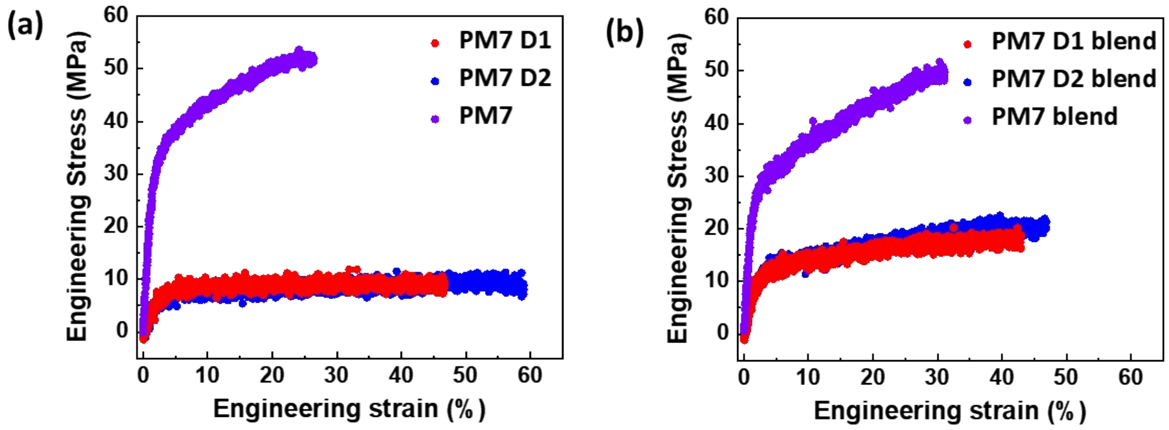


Fig. S6 Stress-strain curves of (a) pristine and (b) blend films.

Table S2 Summary of power conversion efficiencies of all-PSCs and crack onset points of their active layers (measured by pseudo free-standing tensile test) in this work and other works.

Active layers	PCE (%)	Crack onset point (%)	Ref.
PM7 D1:P(NDI2HD-Se)	9.13	43.0	This work
PM7 D2:P(NDI2HD-Se)	6.16	47.1	This work
PM7:P(NDI2HD-Se)	6.64	31.1	This work
PBDTTTPD:P(NDI2HD-T)	6.64	7.2	4
PM6:PF2-DTGe	8.09	6.7	5
PM6:PF2-DTSi	10.77	8.6	5
PM6:PF2-DTC	8.31	11.3	5
PTB7-Th:P(NDI2HD-T2)	6.32	11.6	6
PTzBI:P(NDI2OD-T2)	8.36	15.6	7
PTB7-Th:P(NDI2OD-T2)	4.96	31.1	8
TQ-F:P(NDI2OD-T2)	7.12	32.6	9
PBDB-T:P(NDI2OD-T2)	7.02	38.9	10

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