Supplementary information for

Flexible-Spacer Incorporated Polymer Donors Enable Superior Blend Miscibility for High-Performance and Mechanically-Robust Polymer Solar Cells

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KEYWORDS: polymer solar cell; polymer donor; non-fullerene small-molecule acceptor; mechanical robustness; high efficiency.

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Materials: 4,8-Bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT monomer), 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione (BDD monomer) were purchased from *SunaTech* Incorporation. The FS unit, 1,10-bis(5-bromothiophen-2-yl)decane, was synthesized by the method reported in the literature.[1] Y7 SMA was purchased from *Derthon*. 2,9-bis(3-((3-(dimethylamino)propyl)amino)propyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (PDINN) interlayer was synthesized by following the method in the previous report.[2] All other materials including catalysts were purchased from *Sigma Aldrich*.

Fabrication of polymer solar cell (PSC): The PSC device structure was indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene:polystyrene sulfonic acid) (PEDOT:PSS, AI4083 from Heraeus)/active layer/PDINN/Ag. ITO-coated glass substrates were washed by ultrasonication with acetone and isopropyl alcohol, and dried in an oven at 80 °C. The washed ITO-coated glass was plasma-treated for 10 min and PEDOT:PSS solution was spin-casted (3000 rpm, 30 s). Then, the substrates were thermally annealed (165 °C, 20 min) and moved into a glove-box. The bulk-heterojunction (BHJ) solutions with optimal conditions (20 mg mL^{-1} in chlorobenzene, donor:acceptor = 1:1 and 1 vol% of 1-chloronaphthalene) were spin-coated onto the substrates (2000 rpm, 20 s), and baked at 100 ℃ for 5 min. Next, the PDINN solution (1 mg mL^{-1} in methanol) was casted onto the BHJ layer (3000 rpm, 20 s) and top electrode (Ag, 120 nm) was thermally deposited. The photoactive area for PSC measurement was 0.164 cm^2. The results of more than ten PSC devices were collected for each active system and the average/maximum photovoltaic parameters of the data are presented in **Table 2** to determine data reliability.

Fabrication of flexible polymer solar cell (FPSC): The device fabrication procedures were based on the previous literature.[3] We used thermoplastic polyurethane (TPU) as the substrate because it has high transmittance and bendability. For the bottom electrode, we used PEDOT:PSS (Heraeus Clevios™ PH1000) to replace ITO and included additives to enhance the properties of the PEDOT:PSS. In detail, 5 vol% of dimethyl sulfoxide (DMSO) for better electrical properties, 2 vol% polyethylene glycol (PEG) for better mechanical properties, and 0.5 vol% of Zonyl fluorosurfactant (Zonyl FS-30) as a dopant were added into the PEDOT:PSS solution. The rest of the devices including active layer, electron transporting layer, and electrode were fabricated following the same processes with the PSC fabrication.

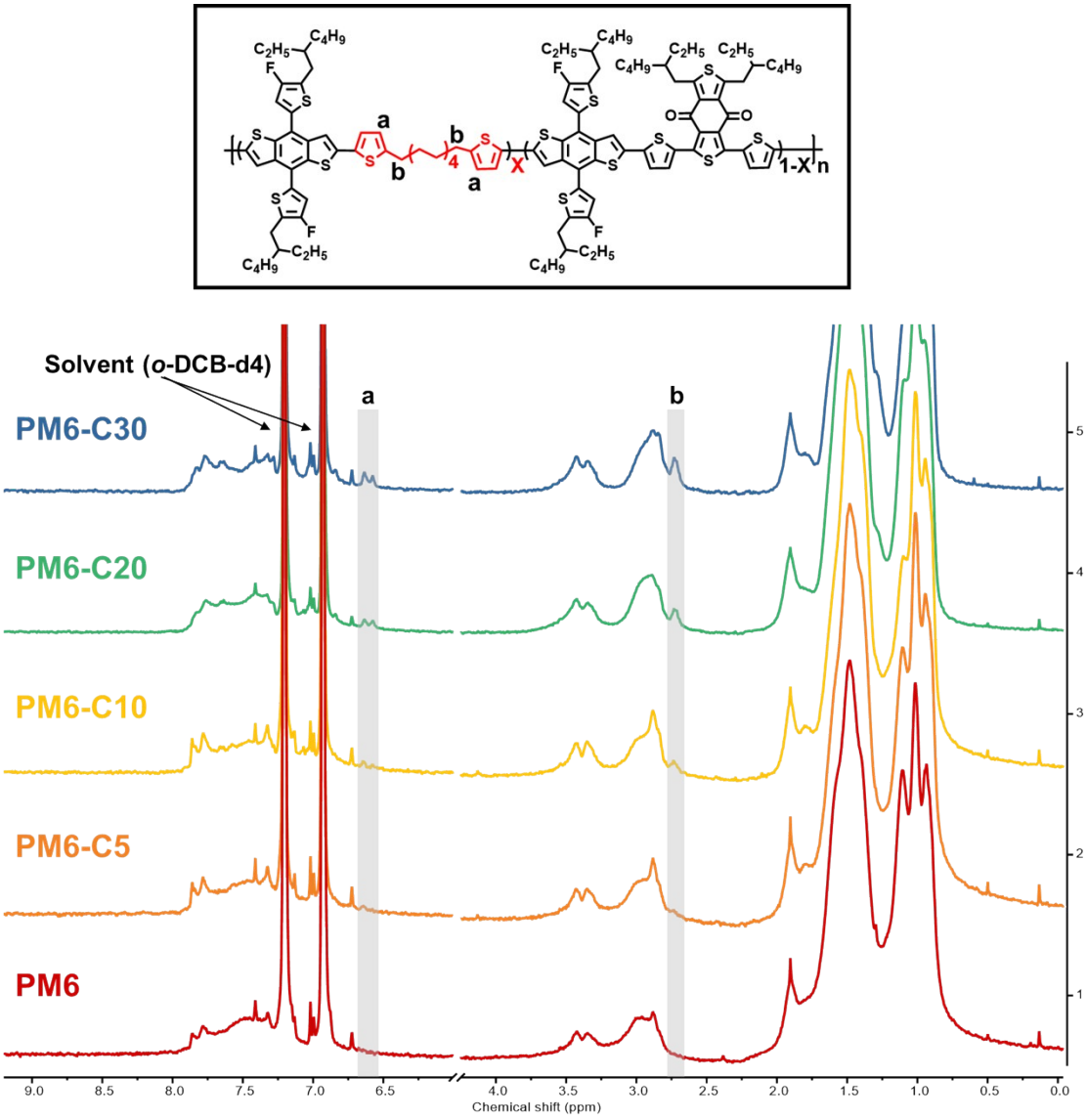

Fig. S1 Collected ^{1}H NMR spectra of PM6-CX P_{D}s.

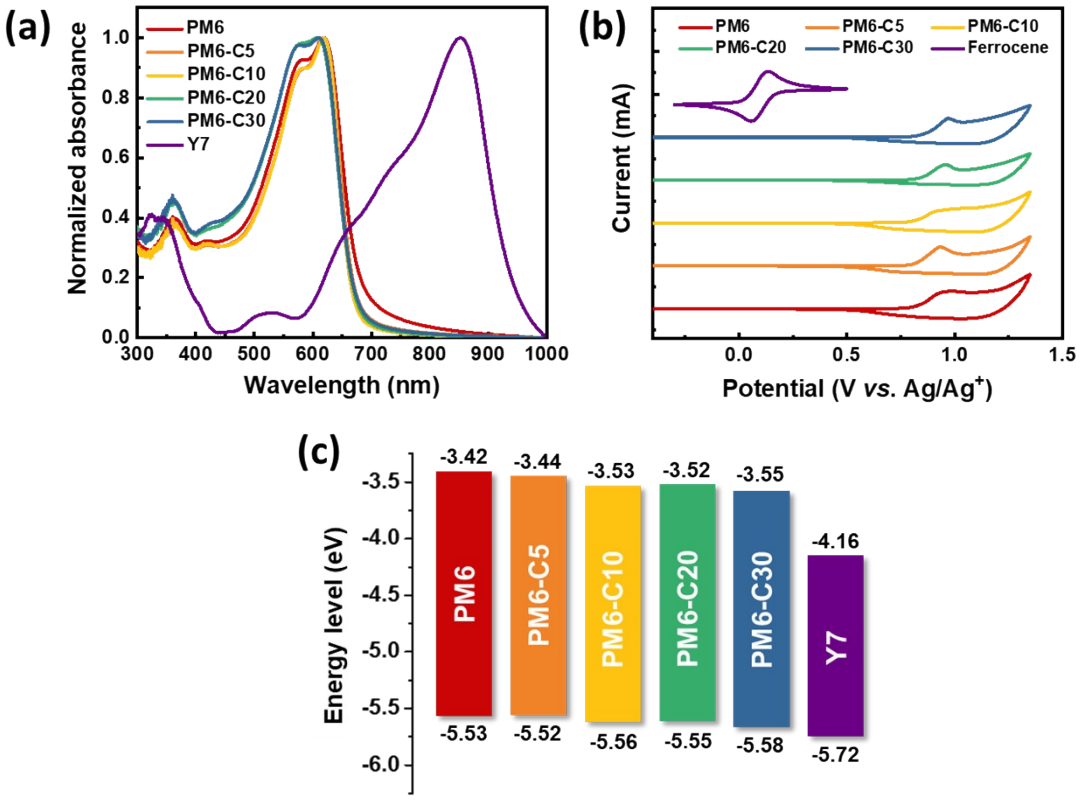

Fig. S2 (a) UV-vis absorption spectra of the P_Ds and Y7 acceptor in film state. (b) Cyclic voltammograms and (c) energy diagrams for the P_Ds in this study.

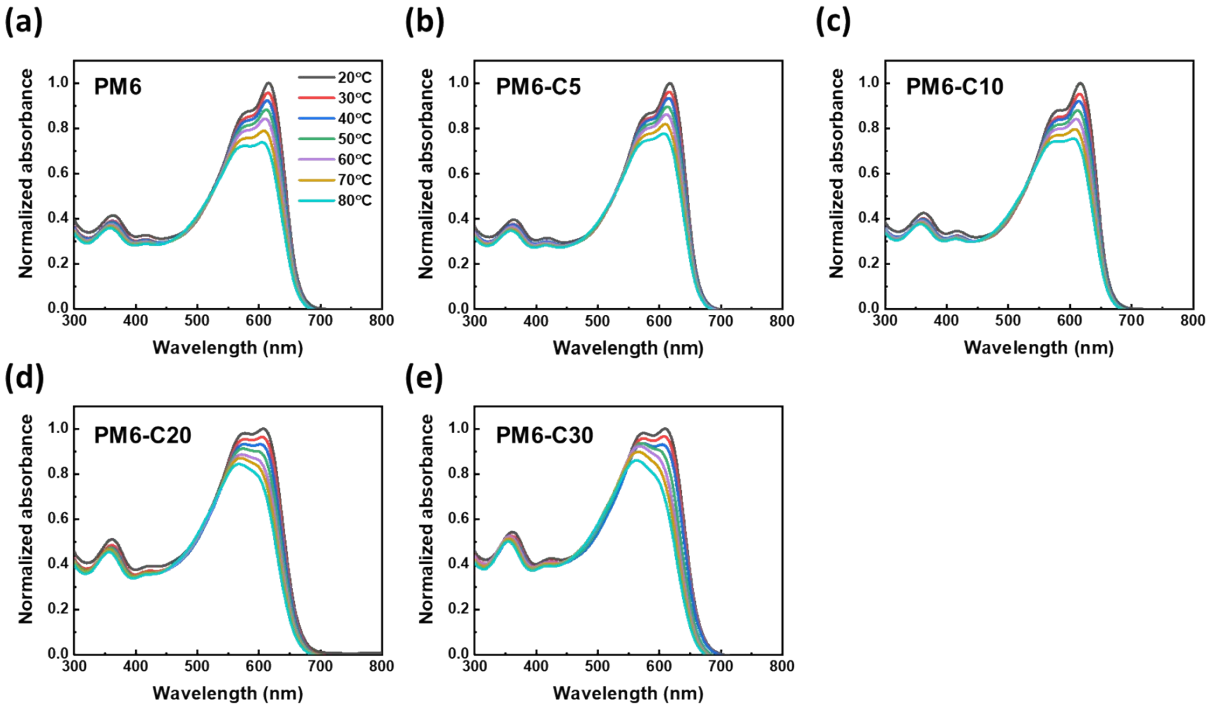

Fig. S3 Temperature-dependent UV-Vis absorption spectra for the pristine P_Ds in chlorobenzene solutions.

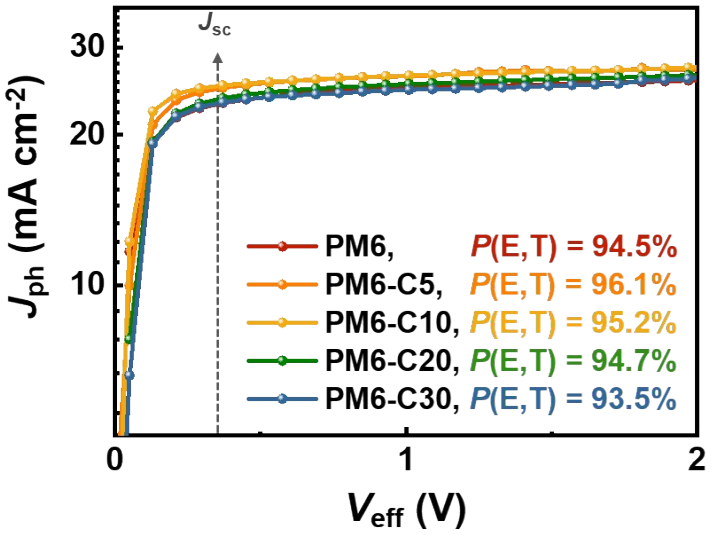

Fig. S4 J_{ph} vs. V_{eff} curves for the P_D:Y7 blends.

Table S1 SCLC mobilities and thickness information for the P_D:Y7 blends.

P_D	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	Thickness (nm)[a]
PM6	1.6×10^{-4}	2.1×10^{-4}	107
PM6-C5	4.0×10^{-4}	2.9×10^{-4}	115
PM6-C10	3.6×10^{-4}	2.0×10^{-4}	110
PM6-C20	8.4×10^{-5}	7.6×10^{-5}	121
PM6-C30	5.3×10^{-5}	6.0×10^{-5}	118

[a]Thicknesses of the blend films are same as those in PSC fabrication.

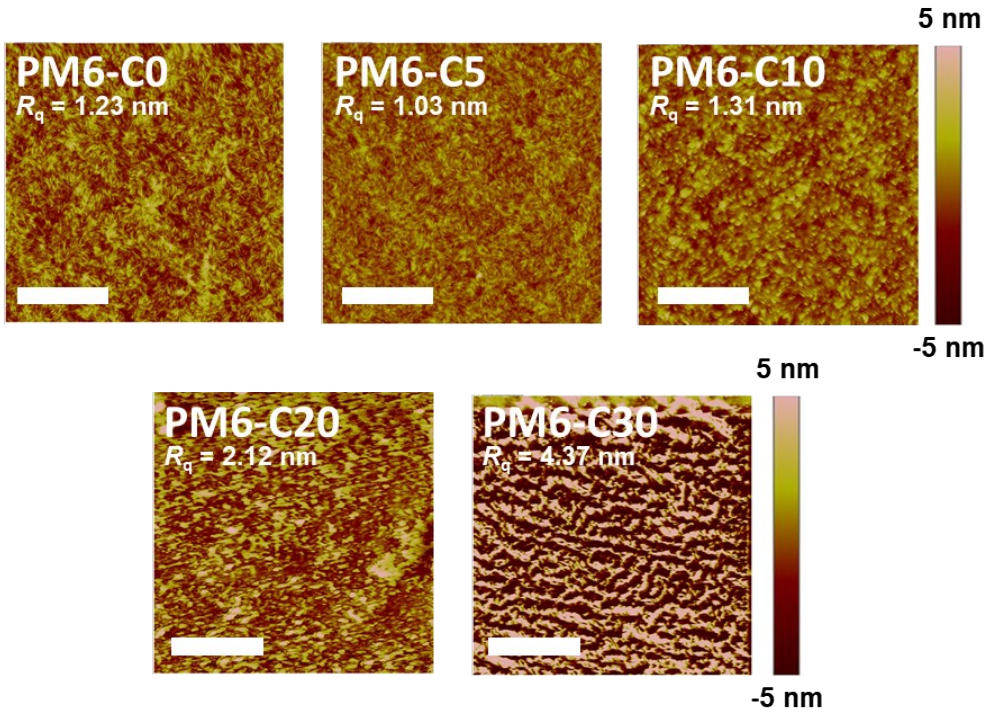

Fig. S5 AFM height images of the P_D:Y7 blends (scale bars are 1 μm).

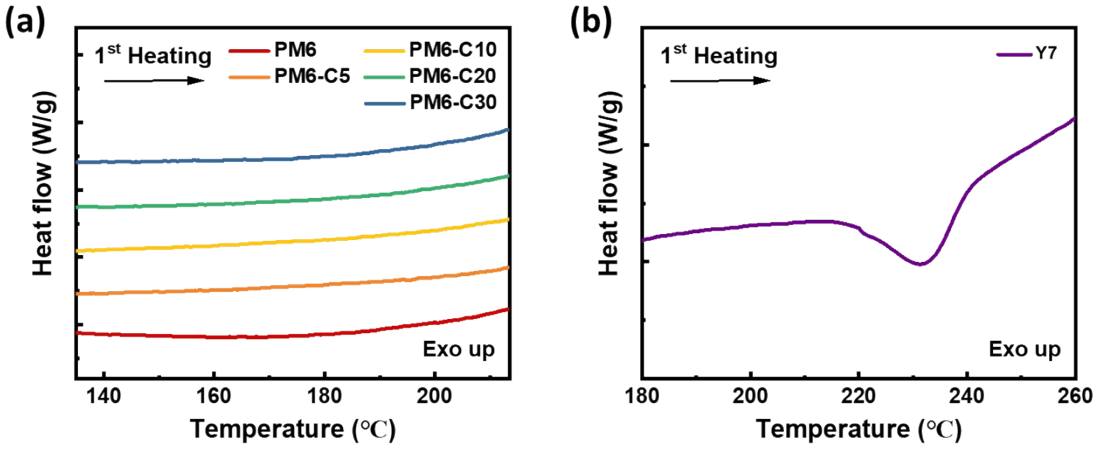

Fig. S6 DSC thermograms of (a) PM6-CX P_Ds and (b) Y7 for the 1st heating cycle.

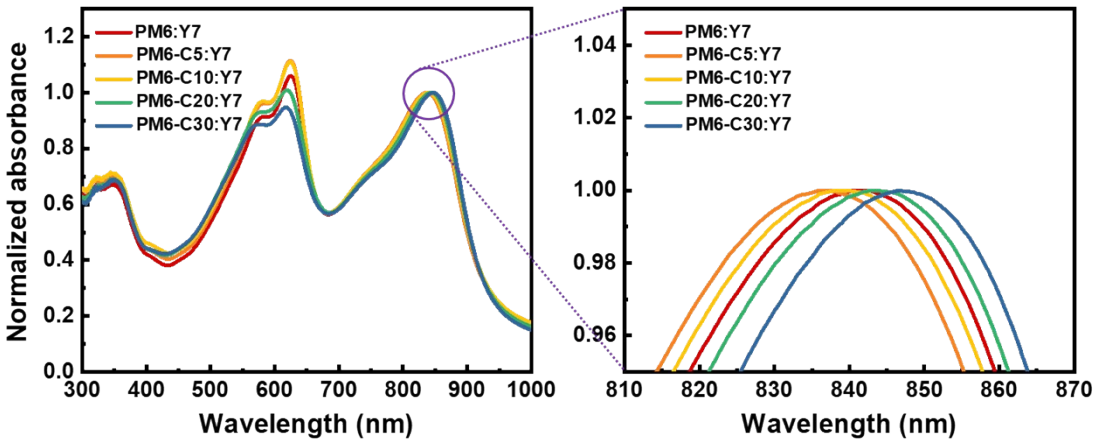

Fig. S7 Normalized UV-vis absorption spectra of the P_D:Y7 blends in film state.

Table S2 λ_{max} values in the lower energy band measured from UV-Vis absorption spectroscopy of the blend films.

P_D	λ_{max} (nm)
PM6-C0	842
PM6-C5	837
PM6-C10	838
PM6-C20	843
PM6-C30	847

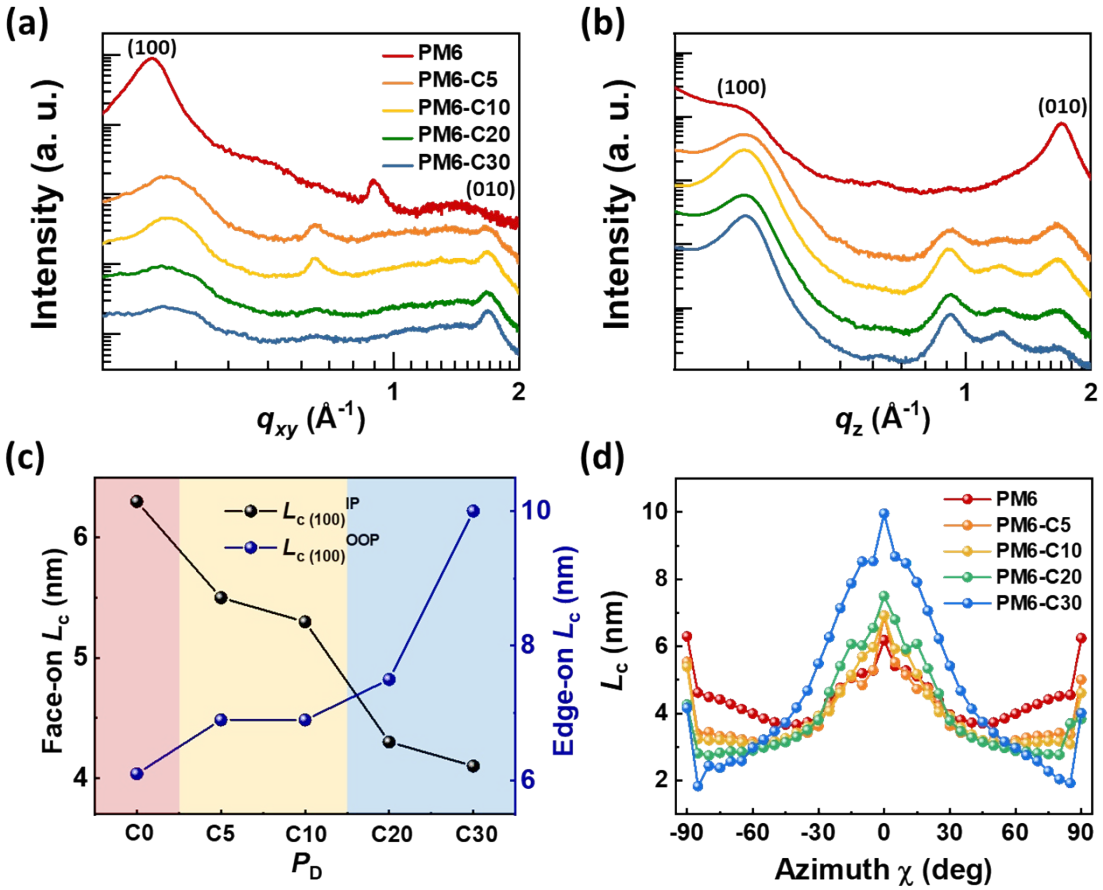

Fig. S8 GIXS linecut profiles of the pristine P_Ds in the (a) IP and (b) OOP directions; (c) coherence length (L_c) values of the (100) scattering peaks for both IP (face-on) and OOP (edge-on) directions depending on the P_Ds; (d) L_c values extracted from (100) scattering peaks at different polar angles.

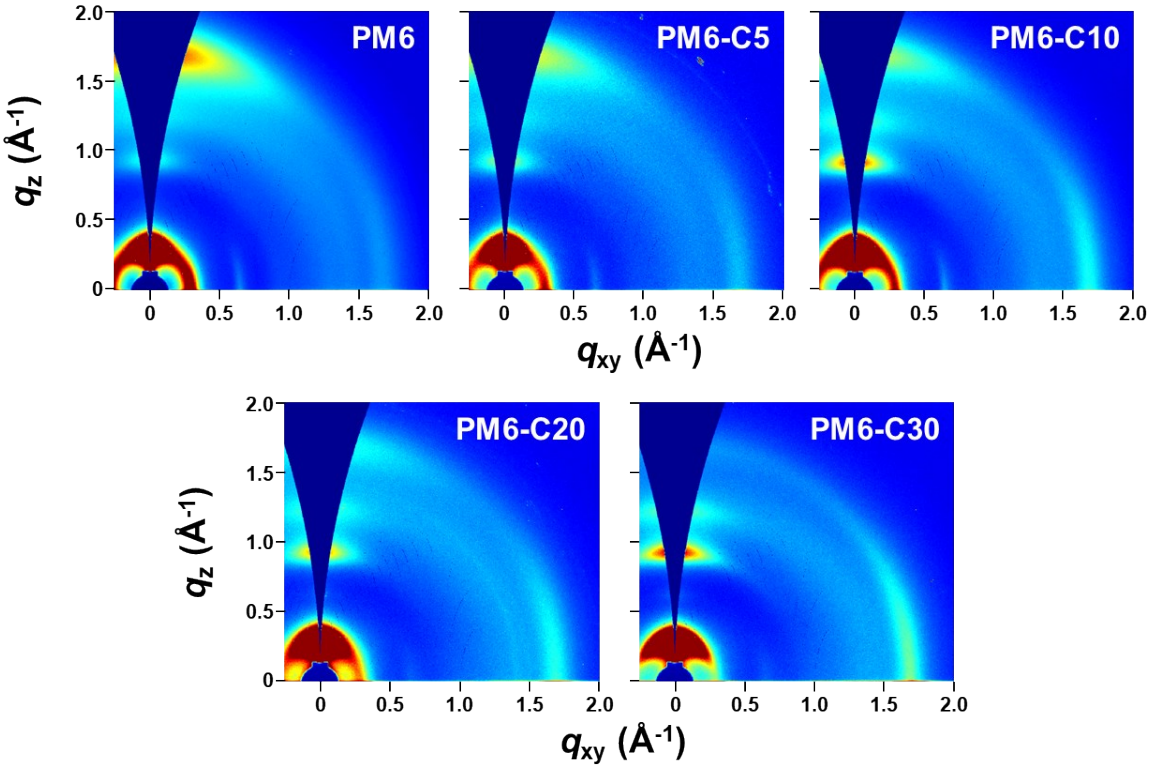

Fig. S9 2D GIXS images of the pristine P_Ds.

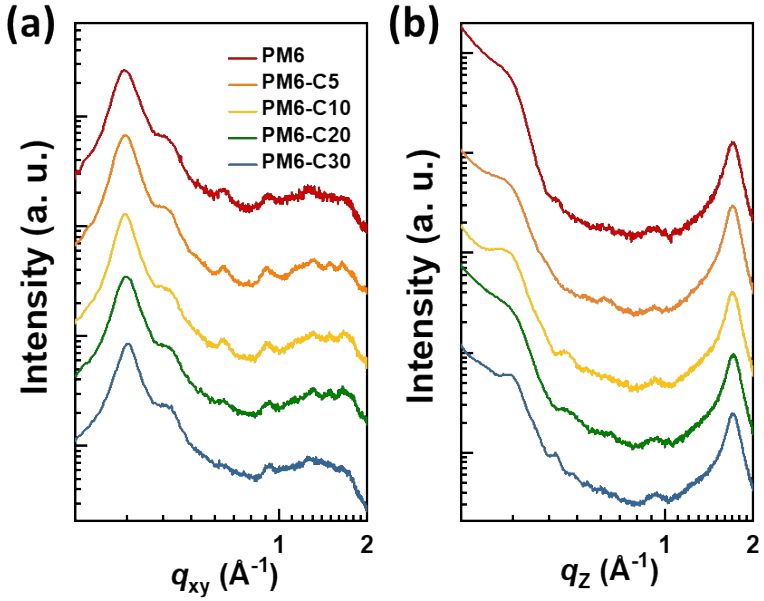

Fig. S10 GIXS linecut profiles for the P_D:Y7 blends in the (a) IP and (b) OOP directions.

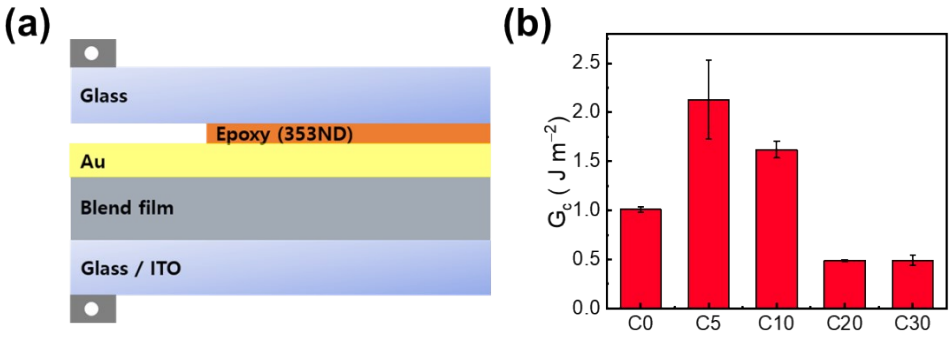

Fig. S11 (a) Sample structure for the DCB tests; (b) G_c values of the blend films depending on the P_Ds.

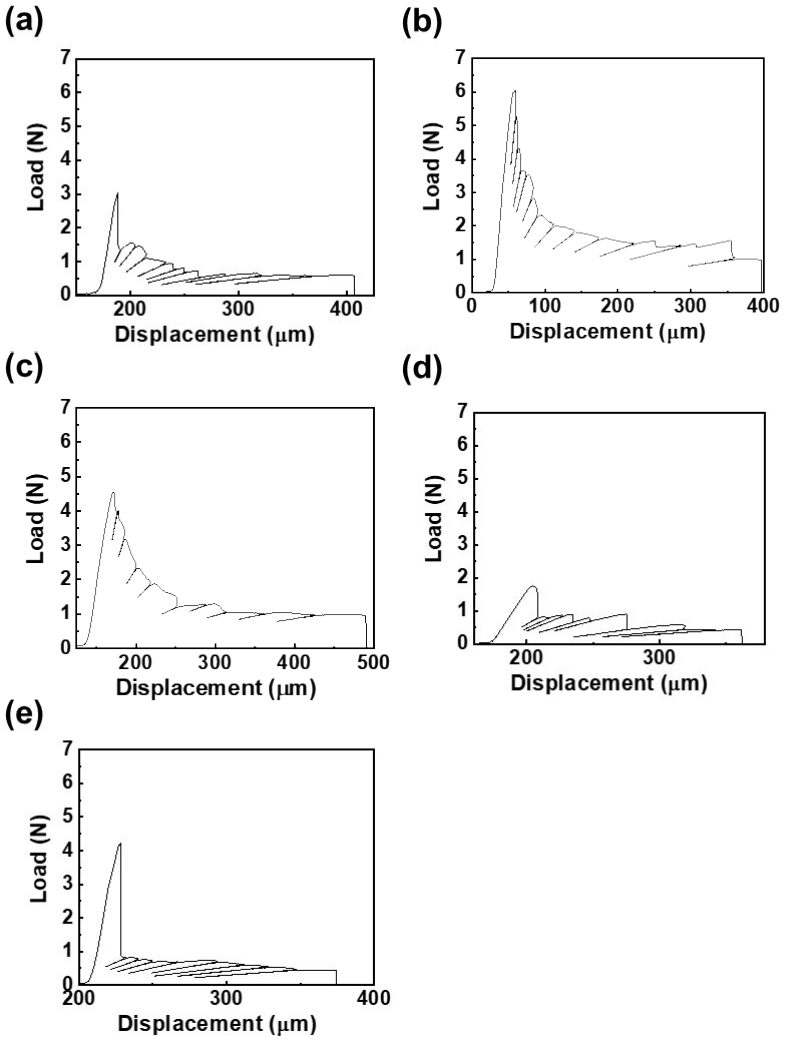

Fig. S12 Load vs. displacement curves from the DCB tests for the blends with (a) PM6, (b) PM6-C5, (c) PM6-C10, (d) PM6-C20 and (e) PM6-C30 P_Ds.

Table S3 PCE and COS values of the binary PSC systems using SMA or SMA-polymerized acceptor in other works and this work.[4-12]

Blend	PCE_{max} (%)	COS (%)[a]	Reference
PM6:IDIC16	4.9	1.4	3
PM6:PF2-DTC	8.3	11.3	3
PM6:PF2-DTSi	10.8	8.6	3
PM6:PF2-DTGe	8.1	6.7	3
PTB7:$PC_{71}BM$ (1:1.5)	0.3	2.1	4
PTB7:$PC_{71}BM$ (1:1)	0.1	4.3	4
PBDTTTPD:$PC_{61}BM$	6.1	0.1	5
PTB7-Th:FOIC (BHJ)	11.0	3.1	6
PTB7-Th:FOIC (P-i-N)	12.0	11.5	6
PTB7-Th:$PC_{71}BM$	6.0	1.1	7
PTB7-Th:ITIC	6.4	3.4	7
PTB7-Th:P-15K	3.1	6.0	7
PTB7-Th:P-20K	3.4	11.2	7
PTB7-Th:$PC_{71}BM$	8.4	1.1	8
PBDB-T:Y5-2BO	7.0	2.3	9
PBDB-T:P(BDT2BOY5-H)	8.8	19.3	9
PBDB-T:P(BDT2BOY5-F)	9.8	16.7	9
PBDB-T:P(BDT2BOY5-Cl)	11.1	15.9	9
PM6:Y6	15.4	5.8	10
PBDB-T:PYT (BHJ)	14.1	8.5	11
PBDB-T:PYT (LbL)	15.2	10.5	11
PM6-C5:Y7	16.7	12.1	This work

[a] The presented COSs stand for the values measured by pseudo free-standing tensile method.

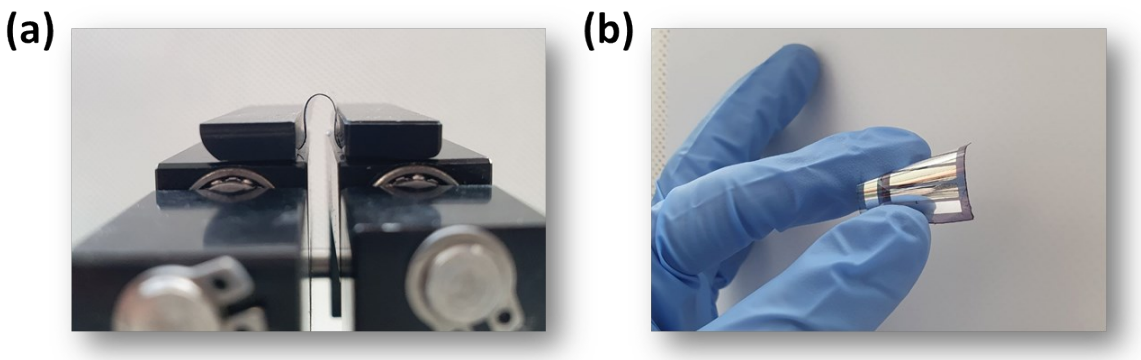

Fig. S13 (a) Experimental setup for the bending tests for the flexible devices, and (b) picture of the flexible devices.

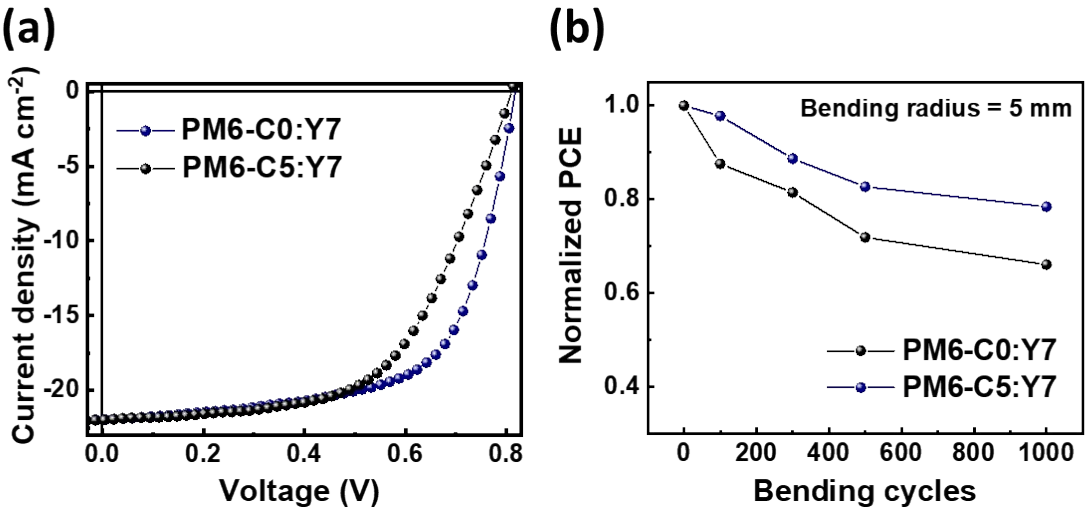

Fig. S14 (a) *J*-*V* curves of the flexible devices without bendings; (b) normalized PCE vs. bending cycles of the P_D:Y7 blends.

Table S4 Photovoltaic parameters of the flexible devices (without bending).

P_D	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
PM6-C0	0.81	21.99	0.58	10.29
PM6-C5	0.82	21.97	0.65	11.64

Table S5 PCE values of the flexible devices depending on the bending cycles.

Cycle / P_D	0	200	500	1000	1500
PM6-C0	10.29	9.01	8.39	7.40	6.81
PM6-C5	11.64	11.39	10.32	9.63	9.14

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