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Supporting Information

Benzobisthiazole-Substituted Terpolymers for Non-Halogenated Solvent-Processed Polymer Solar Cells with Enhanced Efficiency, Thermal Stability and Mechanical Robustness

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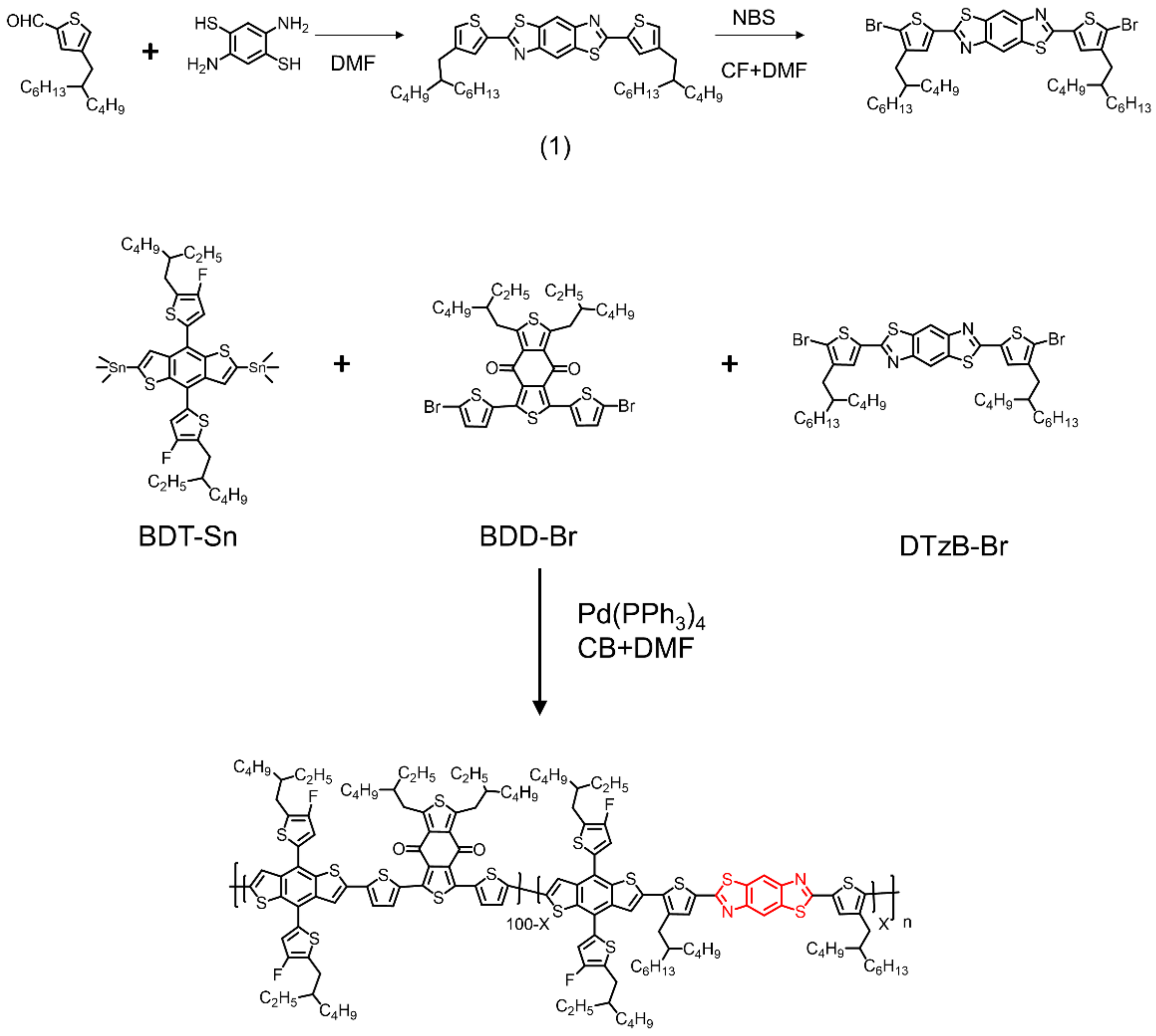
Experimental Section

Materials **:** All materials and chemicals were prepared from Sigma Aldrich Co. and Derthon Co. 2,2'-((2*Z*,2'Z)-((12,13-bis(2-butyloctyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile (Y6-BO) small-molecule acceptor (SMA) was purchased from Derthon Co. and used without further purification. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) solution (Clevios, AI4083) was purchased from Heraeus (Germany) and used as the hole transporting layer of polymer solar cells (PSCs). Poly[(9,9-bis(3′-((*N*,*N*-dimethyl)-nethylammonium)propyl)-2,7-fluorene)-alt-5,5′-bis-(2,2′-thiophene)-2,6-naphthalene-1,4,5,8-tetracaboxylic-*N*,*N*′-di(2-ethylhexyl)imide] dibromide (PNDIT-F3N-Br) was synthesized by following the method reported in the previous paper.[1]

Synthesis of polymer donors (P_{DS})



Scheme 1. Synthetic scheme for DTzB-Br monomer and P_{DS}

(1) Synthesis of DTzB-Br monomer.

The compound 1 was synthesized by following the previously reported paper.[2,3] The compound 1 (500 mg, 0.7 mmol) was dissolved in the mixture of chloroform (30 ml) and *N*, *N*-dimethylformamide (3 ml). The *N*-bromosuccinimide (255 mg, 1.5 mmol) was added to the mixture and stirred overnight at room temperature. The solvent in the mixture was removed under reduced pressure. The residual mixture was purified through a silica-gel packed column using a chloroform/hexane mixture as an eluent. The purified product was obtained as a yellow solid (480 mg, Yield = 78%).

^{1}H nuclear magnetic resonance (NMR) (400 MHz, $CDCl_3$, 298 K) δ 8.40 (s, 2H, aromatic protons), 7.32 (s, 2H, aromatic protons), 2.55 (d, 4H, aliphatic protons), 1.72 (m, 2H, aliphatic protons) 1.31-1.27 (m, 32 H, aliphatic protons), 0.89 (m, 12H, aliphatic protons). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 162.05, 152.35, 143.50, 137.08, 134.81, 130.69, 115.64, 39.29, 35.01, 34.10, 33.79, 32.68, 30.47, 29.53, 27.29, 23.84, 23.49, 14.93

(2) *General polymerization condition of PM6-DTzBX (X=0, 5, 10, 20)*

In a 20 mL reaction vial, BDT-Sn (100 mg, 0.1 mmol) and $Pd(PPh_3)_4$ (0.3 mmol), and BDD-Br (0.1 mmol) for PM6 or a mixture of BDD-Br:DTzB-Br with various ratios (0.095 mmol:0.05 mmol for PM6-DTzB5, 0.09 mmol:0.01 mmol for PM6-DTzB10, 0.08 mmol:0.02 mmol for PM6-DTzB20) were added and purged with Ar gas. The chlorobenzene (6 mL) and *N*, *N*-dimethylformamide (1 mL) were added to the vial and stirred at 110 °C for 6 h. The mixture was precipitated in the methanol and purified through the soxhlet apparatus in the order of methanol, acetone, hexane. The residue was extracted using chloroform and precipitated in the methanol. The polymers were dried under vacuum conditions. The yield of all polymers was higher than 75%.

PSC fabrication and characterization :

The PSCs with a conventional structure (indium tin oxide (ITO)/ PEDOT:PSS/active layer/ PNDIT-F3N-Br/Ag) were prepared with the following procedures. ITO-coated glass substrates were sequentially washed with ultrasonication in order of acetone, deionized water, and isopropyl alcohol. Then, the ITO substrates were dried for 6 h in an oven (70 °C) at an ambient pressure, and then proceeded with plasma treatment for 10 min. The PEDOT:PSS solution (Clevios, AI4083) was spin-coated on the ITO substrates at 3300 rpm for 30 s. Then, the film/substrate was annealed in the air (160 °C, 10 min) before transfer them into an N_2-filled glovebox. The active layer solutions were dissolved in *ortho*-xylene (*o*-xylene) with an optimized condition (donor:acceptor weight ratio = 1:1.2, concentration = 20 mg ml^{-1}, and 1-chloronaphthalene 0.7 vol%), and then stirred at 115 ℃ condition. The solution was cooled down to 90 ℃ and spin-coated onto the PEDOT:PSS/ITO substrates. The thicknesses of active layers of all systems were about 100 nm, measured by the atomic force microscopy (AFM). Then, the substrates were dried with high vacuum ($< 10^{-6}$ torr) for 3 h and annealed at 90 ℃ for 5 min. PNDIT-F3N-Br solution in methanol (1 mg ml^{-1}) was then spin-coated with the condition of 3000 rpm for 30 s. Finally, Ag was deposited with thickness of 120 nm under high vacuum ($\sim10^{-6}$ Torr) in an evaporation chamber. Keithley 2400 SMU instrument was used to measure the power conversion efficiencies (PCEs) under an Air Mass 1.5 G solar simulator (100 mW cm^{-2}, solar simulator: K201 LAB55, McScience), satisfying the Class AAA, ASTM Standards. K801SK302 of McScience was used as a standard silicon reference cell to calibrate the exact solar intensity. The reference cell was calibrated every 3 month. K3100 IQX, McScience Inc. instrument was used to analyze the external quantum efficiency (EQE) spectra, equipped with a monochromator (Newport) and an optical chopper (MC 2000 Thorlabs)

Characterizations: The ^{1}H NMR and ^{13}C NMR spectra of compounds were measured using AV300 MHz NMR instrument (Bruker) using chloroform-d as solvent. The ^{1}H NMR spectra of polymer donors were measured using AV 500 MHz NMR at a temperature of 80 ℃ 1,1,2,2-tetrachloroethane-d_2 as solvent. The M_n and $Đ$ of P_Ds were measured using gel permeation chromatography (GPC) using 140 °C heated 1,2,4-trichlorobenzene as eluent solvent, calibrated with a polystyrene standard. Aggregation properties of materials at dilute solutions and thin films were measured by UV-1800 spectrophotometer. The energy levels of P_Ds and ferrocene were measured using cyclic voltammetry using EC-Lab software with the VSP (BioLogic Science Instruments). The absorption coefficients of P_Ds were calculated using Beer-Lambert law and the thickness values of neat P_D films were measured using AFM. The topology and thickness of blend films were measured by AFM, using NX10 instrument from Park Systems. The 3C beamline at Pohang Accelerator Laboratory was used for measuring grazing incidence X-ray scattering (GIXS) profiles of neat P_D films and P_D:Y6-BO blend films. The incidence angles of X-ray used in GIXS measurement were all same for 0.12 ^{o}. BL 11.0.1.2 in the Advanced Light Source (USA) was used for the measurement of resonant soft X-ray scattering (RSoXS) with a beam energy of 285.0 eV. In-situ UV–Vis absorption spectra profiles of P_D:Y6-BO blends were estimated at every 0.06 s using an HRR2000+CG spectrometer with a DH2000-BAL balanced deuterium tungsten light source.

G(E,T) calculation:

The saturated photocurrent density (J_{sat}) is determined from dependence of the photocurrent denstiy (J_{ph}) on the effective voltage (V_{eff}) under illumination. The exciton dissociation probability (P(E,T) of each PSC was calculated by measuring J_{sat} at V_{eff} = 2 V. The G_{max} value is obtained using following equation, assuming that there is no recombination:

$$J_{sat} = q\, G_{max}\, L$$

where q is the electronic charge and L is the active layer thickness.

The free charge carrier generation rate (G(E,T)) can be obtained from the exciton dissociation probability (P(E,T)) and the maxmimum exciton generation rate (G_{max}) as follows:

$$G(\mathrm{E,T}) = G_{max} \times P(\mathrm{E,T})$$

Space-charge-limited current (SCLC) measurements : Hole mobilities of neat P_D films and blend films, and electron mobilities of the blend films were measured using the SCLC method. The device structure for measuring electron mobility was ITO/zinc oxide/active layer/PFN-Br/Al. ITO/PEDOT:PSS/pristine P_D layer or active layer)/Au structure was used for the hole mobility measurement. The neat P_D films were prepared by dissolving P_Ds in *o*-xylene at 7 mg mL^{-1} concentration, and spin-coated with 1000 rpm. The P_D:Y6-BO blend films were prepared by the same conditions for the PSC fabrication. A voltage range from 0 to 6 V was applied to gauge the current-voltage measurements, and then fitted by the Mott-Gurney equation.

$$J_{\mathrm{SCLC}} = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{L^3}$$

where ε_0 represents the permittivity of free space (8.85×10^{-14} F cm^{-1}), ε is the relative dielectric constant of the polymer films, μ is the mobility of the charge carrier, V is the calculated potential across the SCLC device ($V = V_{\mathrm{applied}} - V_{\mathrm{bi}} - V_{\mathrm{r}}$, which V_{bi} is the potential of built-in state and V_{r} is the degree of voltage drop), and L is the film thickness.

Contact angle measurements and interfacial tension calculation: Contact angles of the materials were measured using a Contact Angle Analyzer (Phoenix 150, SEO, Korea). The surface tension of the thin-films was determined using the Wu model, which utilized contact angle measurements from both water and glycerol on neat films. The calculation method is described in detail below:

$$\gamma_{\mathrm{water}}(1 + \cos\theta_{\mathrm{water}}) = \frac{4\gamma_{\mathrm{water}}^{\mathrm{d}}\gamma^{\mathrm{d}}}{4\gamma_{\mathrm{water}}^{\mathrm{d}} + 4\gamma^{\mathrm{d}}} + \frac{4\gamma_{\mathrm{water}}^{\mathrm{p}}\gamma^{\mathrm{p}}}{4\gamma_{\mathrm{water}}^{\mathrm{p}} + 4\gamma^{\mathrm{p}}} \qquad (1)$$

$$\gamma_{\mathrm{GC}}(1+\cos\theta_{\mathrm{GC}}) = \frac{4\gamma_{\mathrm{GC}}^{\mathrm{d}}\gamma^{\mathrm{d}}}{4\gamma_{\mathrm{GC}}^{\mathrm{d}} + 4\gamma^{\mathrm{d}}} + \frac{4\gamma_{\mathrm{GC}}^{\mathrm{p}}\gamma^{\mathrm{p}}}{4\gamma_{\mathrm{GC}}^{\mathrm{p}} + 4\gamma^{\mathrm{p}}} \tag{2}$$

$$\gamma_{\mathrm{total}} = \gamma^{\mathrm{d}} + \gamma^{\mathrm{p}} \tag{3}$$

where γ_{total} = total surface tension, γ_{d} = dispersion component, γ_{p} = polar component, and θ = the contact angle of water or glycerol.

Then, the interfacial tension values between P_{D} and Y6-BO were calculated based on the surface tensions, using the equation below:

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^{\mathrm{d}}\gamma_2^{\mathrm{d}}}{\gamma_1^{\mathrm{d}} + \gamma_2^{\mathrm{d}}} - \frac{4\gamma_1^{\mathrm{p}}\gamma_2^{\mathrm{p}}}{\gamma_1^{\mathrm{p}} + \gamma_2^{\mathrm{p}}} \tag{4}$$

(γ_{12} = interfacial tension between two different materials, γ_{j} (j = 1 or 2) = surface tension of each material, $\gamma_{\mathrm{j}}^{\mathrm{d}}$ = dispersion component of the surface tension, and $\gamma_{\mathrm{j}}^{\mathrm{p}}$ = polar component of the surface tension)

Calculation of relative degree of crystallinity (rDoC)

The most commonly used method that estimates rDoC is to integrate the intensity of the complete pole figure from out-of-plane direction to in-plane direction based on a corrected Ewald sphere. The polar angle (ω) is defined as the angle between the scattering vector and the q_z direction (substrate normal). To calculate rDoC of (010) π–π stacking peak in P_{D}:DSMA blends, we get the pole figures (intensity × sin (ω) versus ω) after background subtraction and normalization for the sample volume. Then, the complete intensity of a selected peak over all orientations is integrated, and the intensity correction is executed. The rDoC can be obtained by using Equation (5).

$$\text{rDoC} \propto \int_0^{\frac{\pi}{2}} sin(\omega)I(\omega)d\omega \qquad (5)$$

where $I(\omega)$ is the scattering intensity at a given orientation angle and sin (ω) is the geometrical correction factor.

***Pseudo free-standing tensile test*:** In the pseudo free-standing tensile method, the blend films were prepared under the same condition as the PSC fabrications. The P_D pristine films were prepared under the same condition as the SCLC hole-only films. All films were spin-coated with the similar thickness (~100 nm). The thickness of sample was measured using AFM. The films were spin-casted onto the polystyrene sulfonic acid (PSS)-coated glass substrate, and cut into a dog-bone shape by a femtosecond laser. PSS layer was spin-coated as sacrifical layer during floating on water due to its higher solubility in water. Since PSS readily dissolves in water, only the sample film was floated onto the water surface and was attached to the grips through Van-der Waals interactions. The strain was applied with a fixed strain rate (0.8×10^{-3} s^{-1}), and the tensile load values were measured by a load cell with high resolution (LTS-10GA, KYOWA, Japan). Elastic modulus (E) was calculated using the least square method for the slope of the linear region in the stress-strain curve within 0.5% strain.

Supplementary Figures & Tables

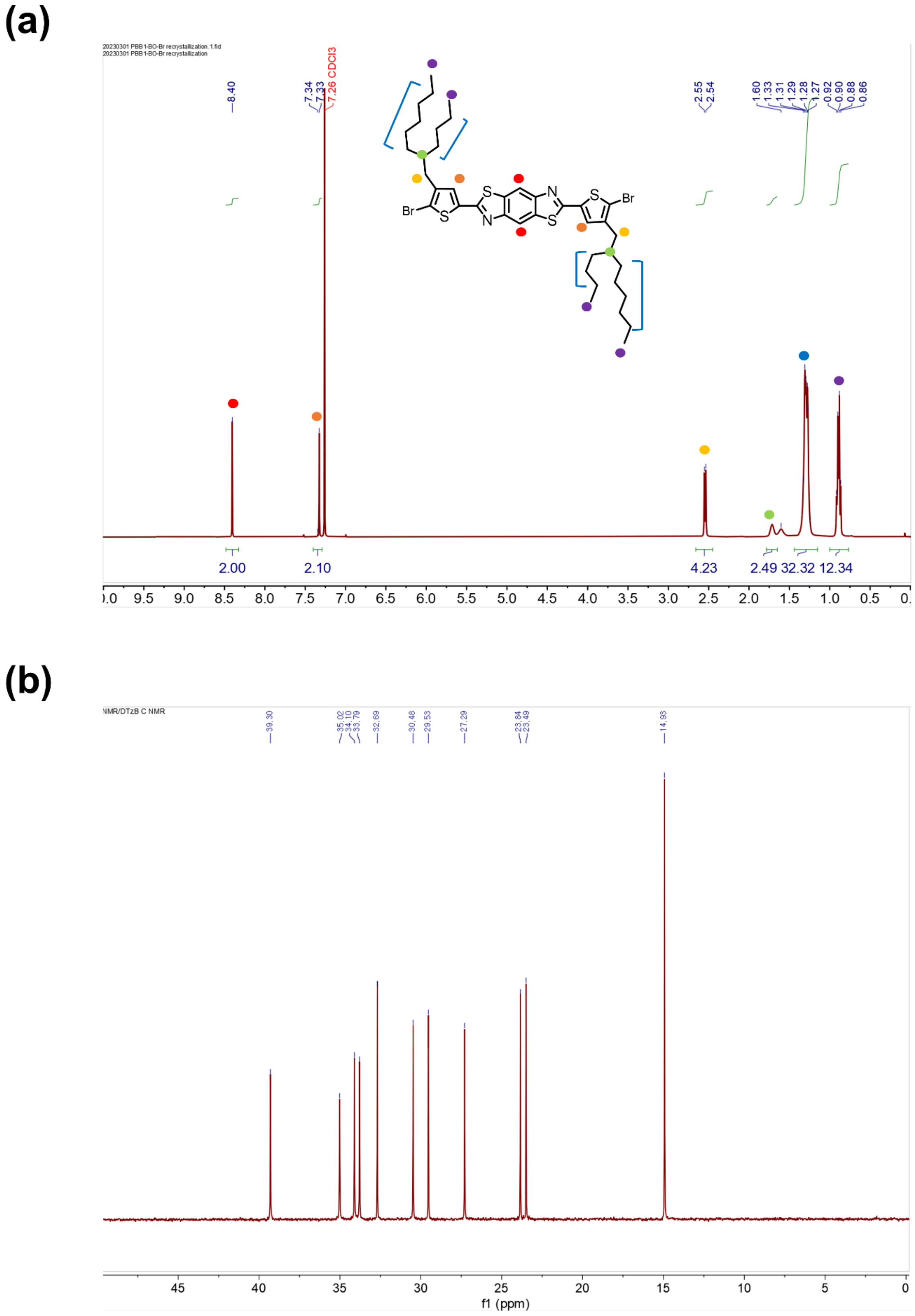


Fig. S1. (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of DTzB-Br monomer.

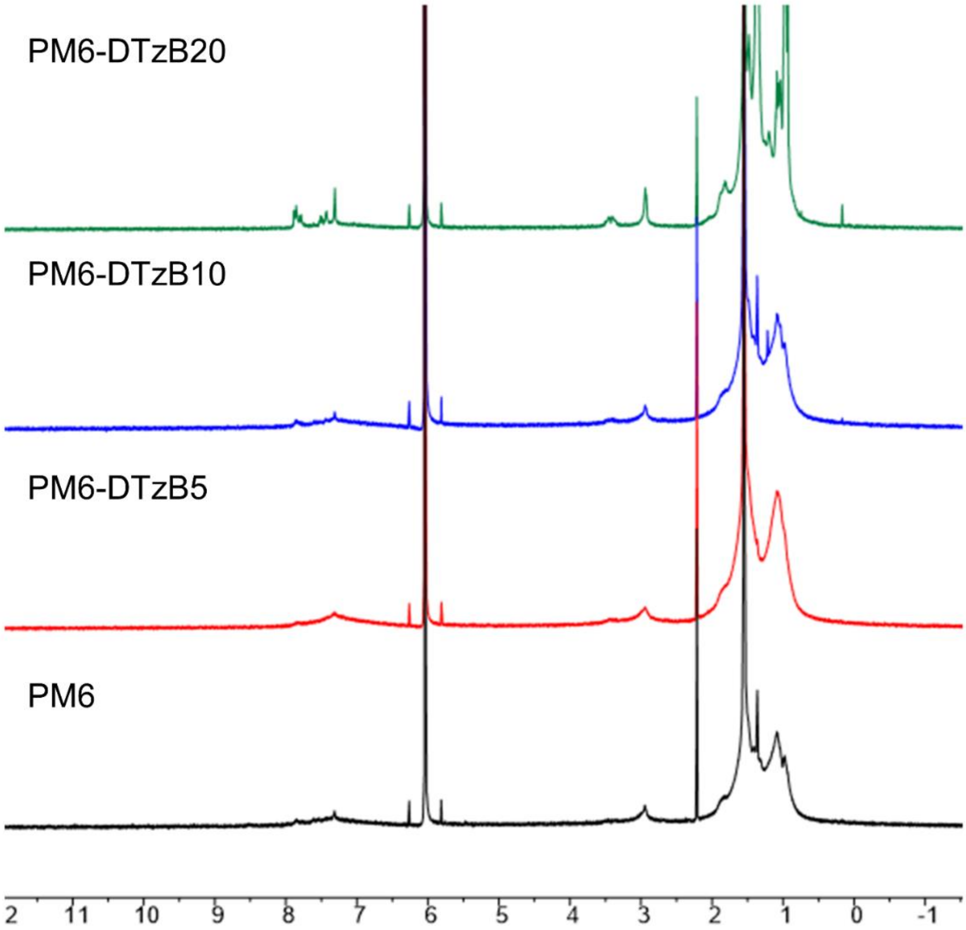


Fig. S2. ^{1}H-NMR spectra of P_{D}s.

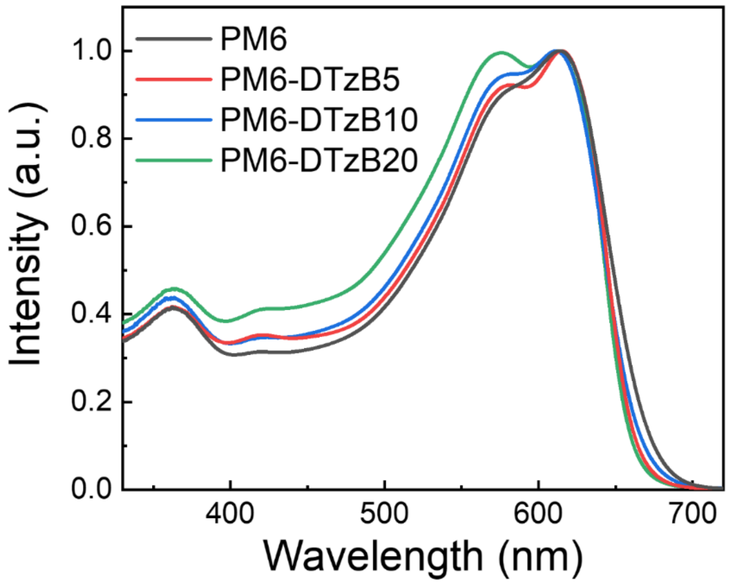


Fig. S3. UV–vis spectra of P_{D}s in dilute solution state dissolved in *o*-xylene.

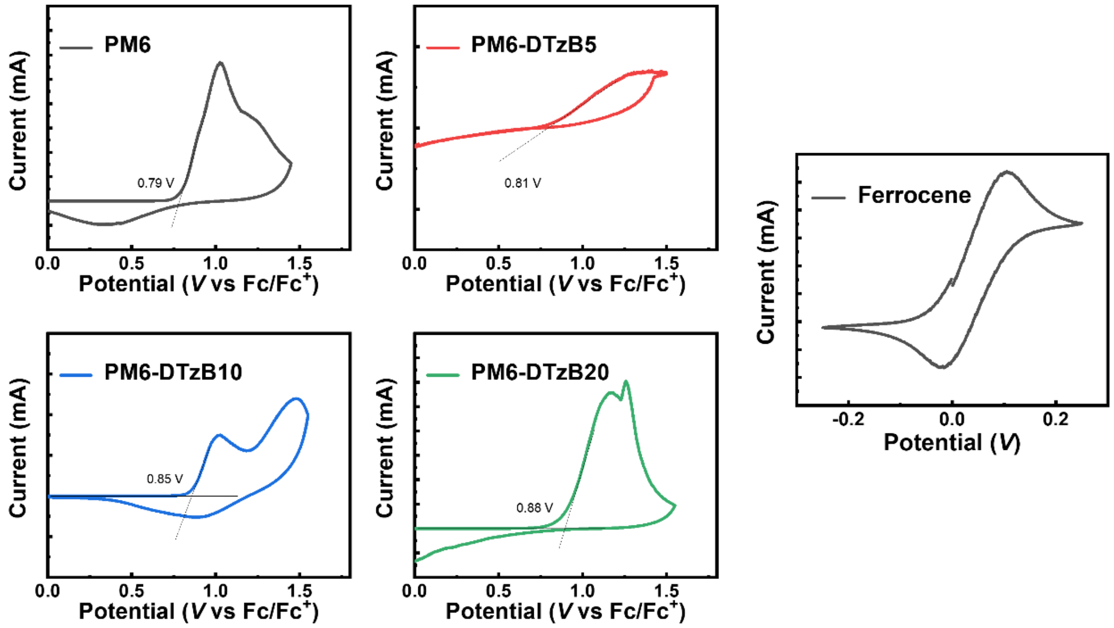


Fig. S4. Cyclic voltammetry of P_{D}s and ferrocene reference.

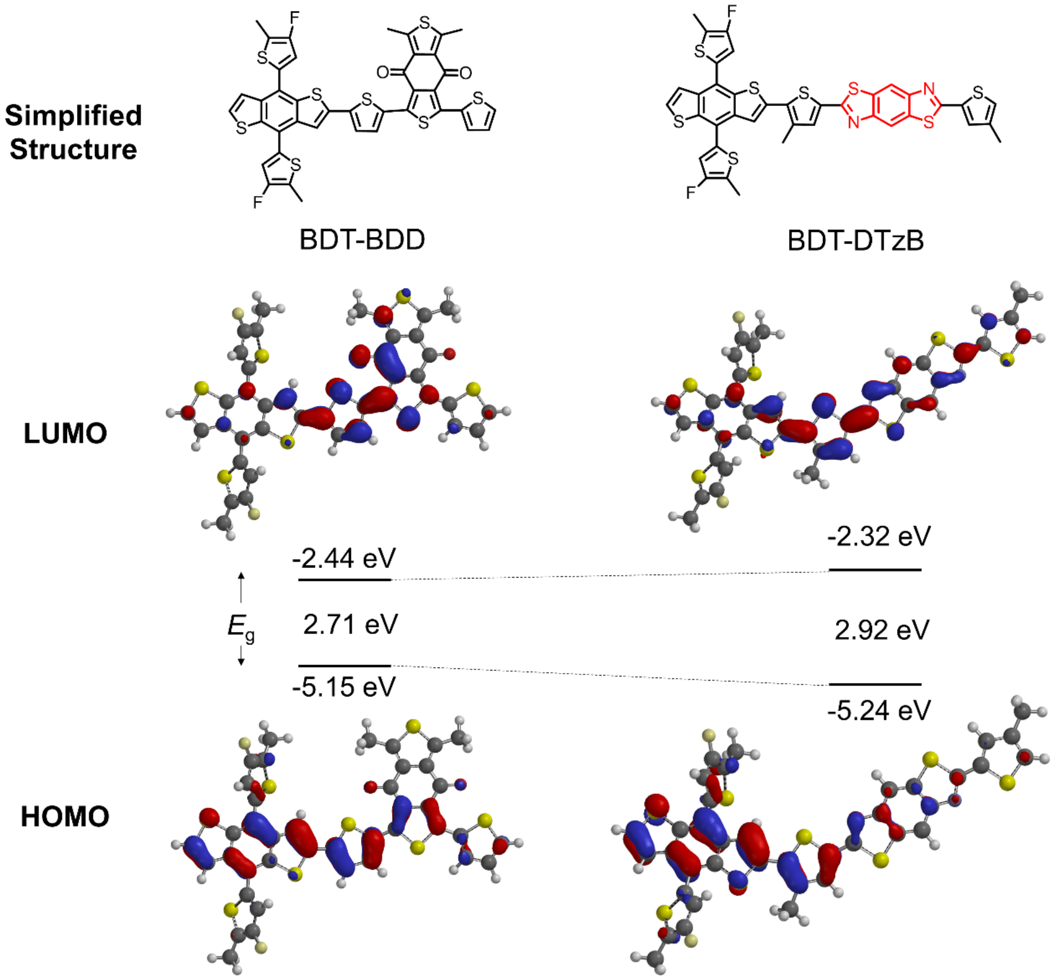


Fig. S5. Density functional theory of simplified structure and calculated energy levels at B3LYP/6-31G(d,p) level. The side chains were simplified as methyl fuction.

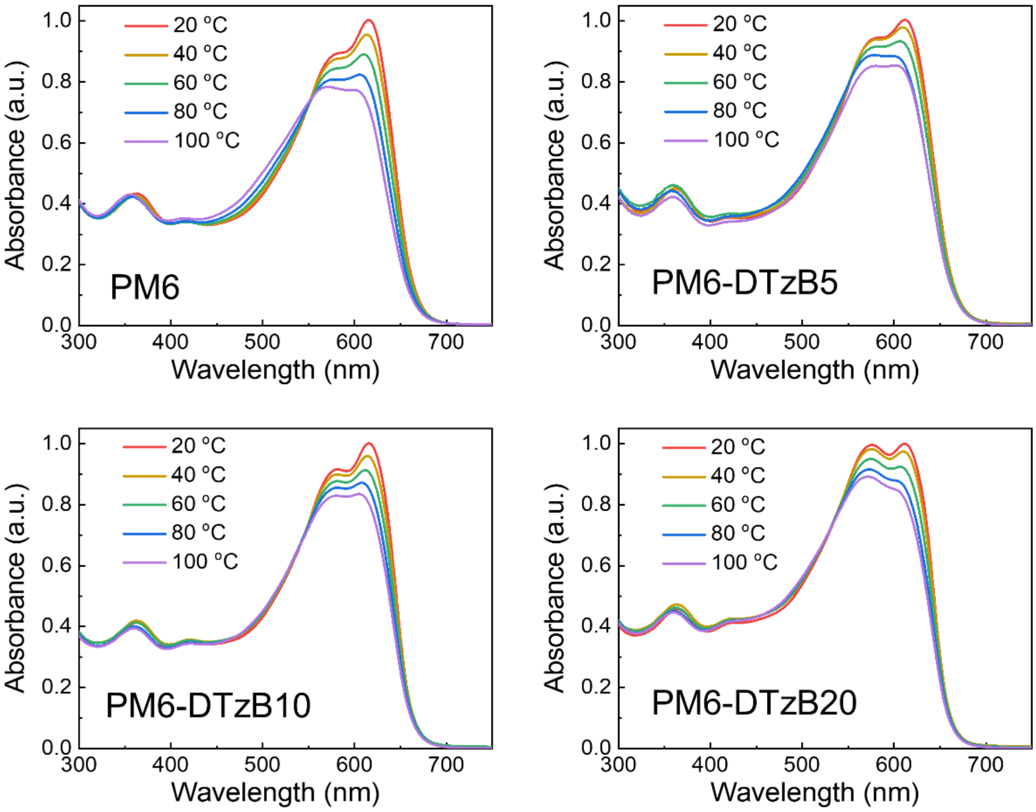


Fig. S6. Temperature-dependent UV–vis absorption spectra of pristine P_D solutions dissolved in *o*-xylene.

Table S1. Intensity ratio of the maximum intensity peaks of the P_Ds under the 20 °C and 100 °C conditions.

P_D	$I_{max}^{100\ ^{o}C}$ / $I_{max}^{20\ ^{o}C}$
PM6	0.77
PM6-DTzB5	0.85
PM6-DTzB10	0.84
PM6-DTzB20	0.88

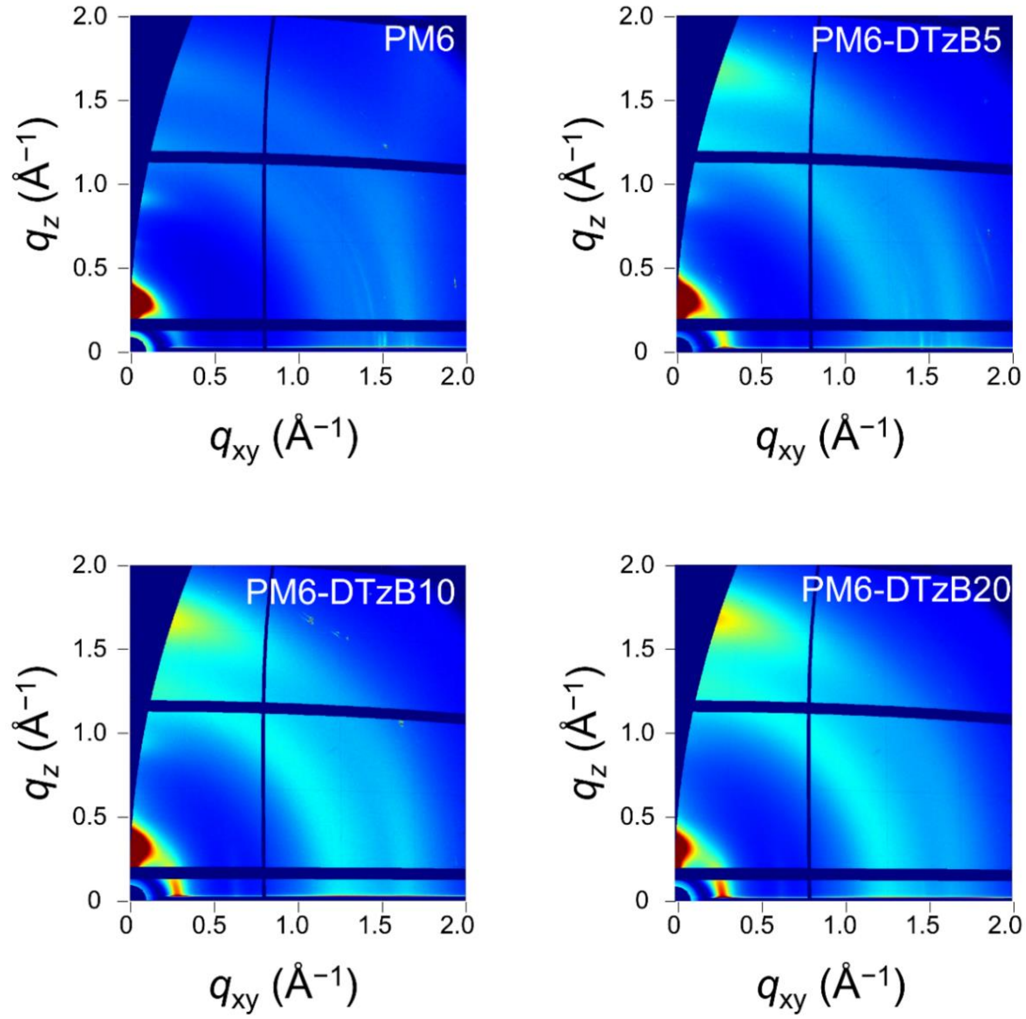


Fig. S7. 2D GIXS images of pristine (a) PM6, (b) PM6-DTzB5, (c) PM6-DTzB10 and (d) PM6-DTzB20 films.

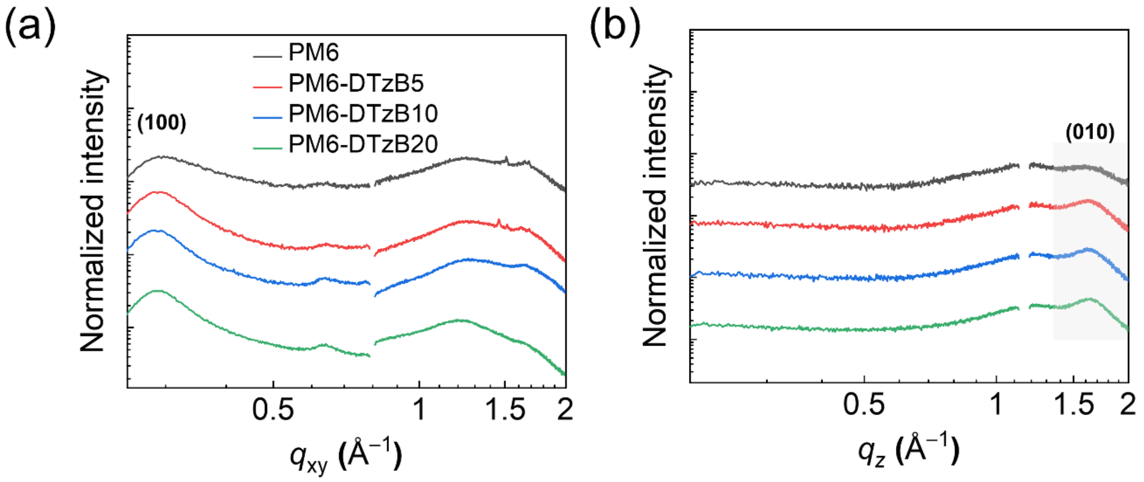


Fig. S8. GIXS linecut of neat P_D films along the (a) in-plane direction and (b) out-of-plane direction.

Table S2. Domain spacing (d) and coherence length (L_c) values of (010) peak along the OOP direction, which were estimated from GIXS line-cut profiles of neat P_D films.

P_D	d_{010} [Å]	$L_{c(010)}$ [nm]
PM6	3.97	0.6
PM6-DTzB5	3.95	1.1
PM6-DTzB10	3.94	1.2
PM6-DTzB20	3.92	1.3

Table S3. SCLC hole mobility of pristine P_{D} films.

P_{D}	μ_{h} [$\times10^{-4}$ cm^2 V^{-1} s^{-1}]
PM6	1.36
PM6-DTzB5	1.48
PM6-DTzB10	1.63
PM6-DTzB20	1.72

Table S4. G_{max}, P(E,T) and G(E,T) of P_{D}:Y6-BO-based PSCs.

P_{D}	G_{max} [× 10^{22} cm^{-3} s^{-1}]	P(E,T) [%]	G(E,T) [× 10^{22} cm^{-3} s^{-1}]
PM6	1.81	98.4	1.79
PM6-DTzB5	1.89	96.7	1.82
PM6-DTzB10	1.97	96.2	1.89
PM6-DTzB20	1.94	95.6	1.86

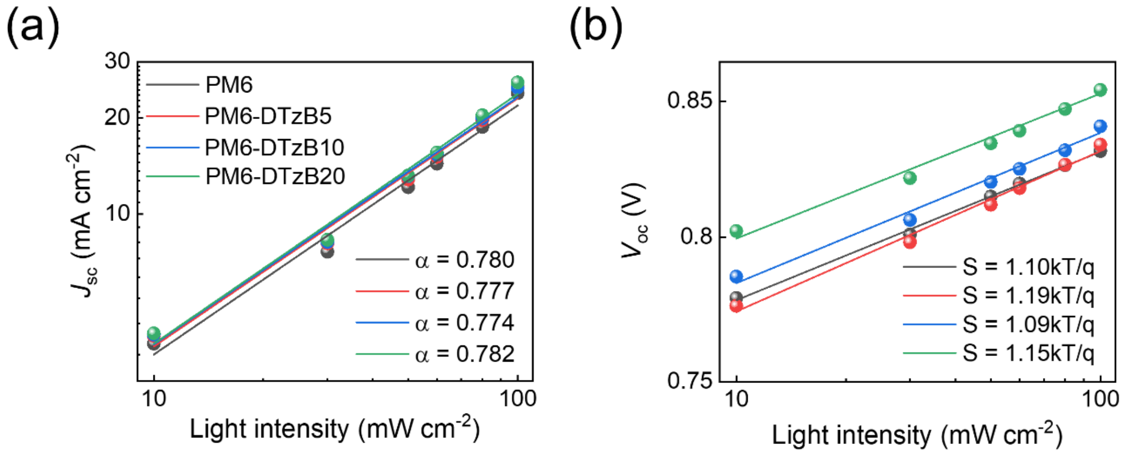


Fig. S9. Light intensity dependent (a) J_{sc} and (b) V_{oc} of PSCs featuring P_{D}:Y6-BO blends.

Table S5. SCLC hole and electron mobilities of P_D:Y6-BO blend films.

P_D	μ_h [$\times10^{-4}$ cm^2 V^{-1} s^{-1}]	μ_e [$\times10^{-4}$ cm^2 V^{-1} s^{-1}]	$\mu_\mathrm{h}/\mu_\mathrm{e}$
PM6	2.14	1.20	1.78
PM6-DTzB5	2.22	1.37	1.62
PM6-DTzB10	2.32	1.55	1.50
PM6-DTzB20	2.12	1.31	1.72

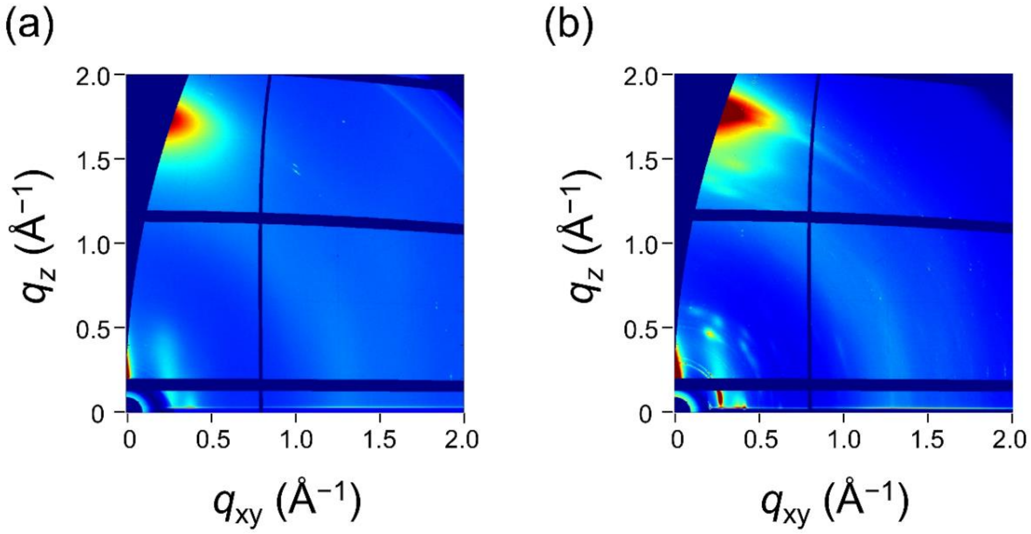


Fig. S10. 2D GIXS images of neat Y6-BO films (a) before and (b) after 90 ºC annealing.

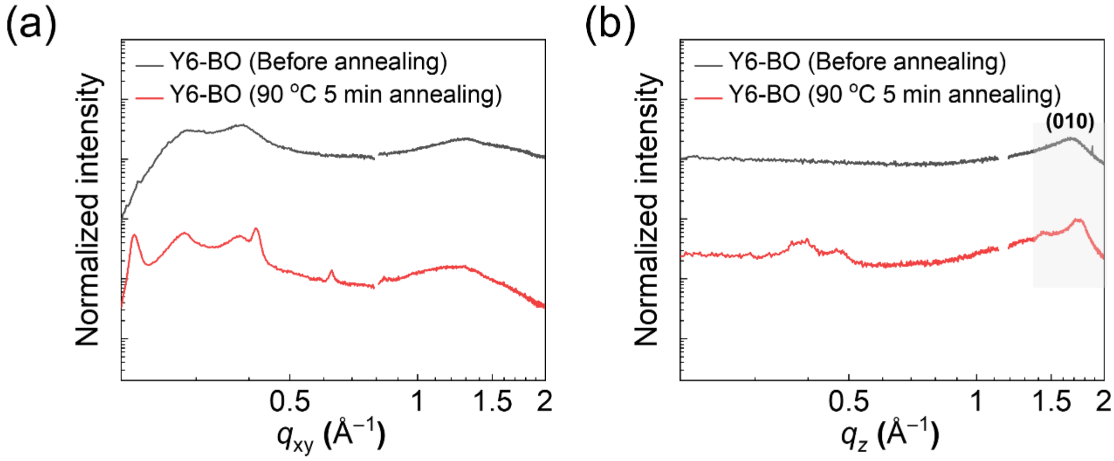


Fig. S11. GIXS line-cut profiles of neat Y6-BO SMA films along the (a) in-plane direction and (b) out-of-plane direction. Red line indicates the lincut profile of the annealed film. The annealing condition was the same for the PSC fabrication.

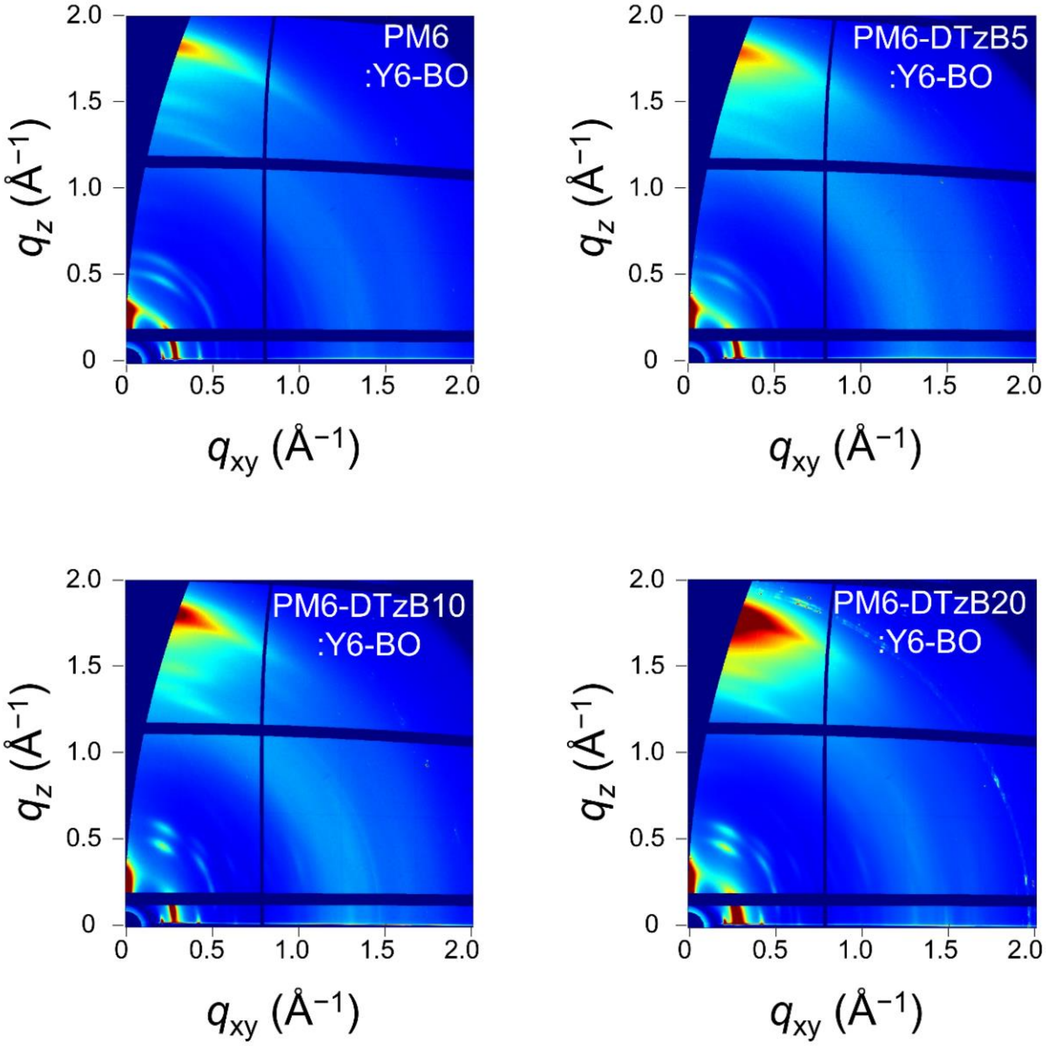


Fig. S12. 2D GIXS images of P_D:Y6-BO blend films.

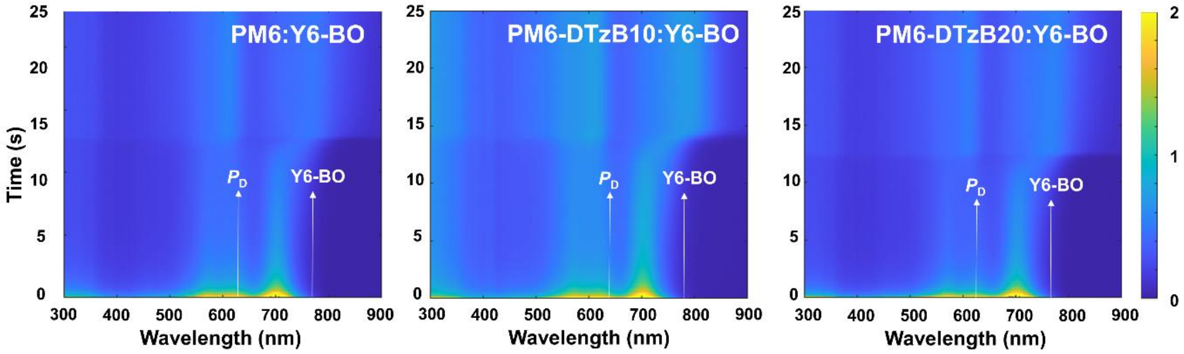


Fig. S13. 2D contour maps of in-situ UV–vis spectra of P_D:Y6-BO blends obtained during the spin-coating process using *o*-xylene solution.

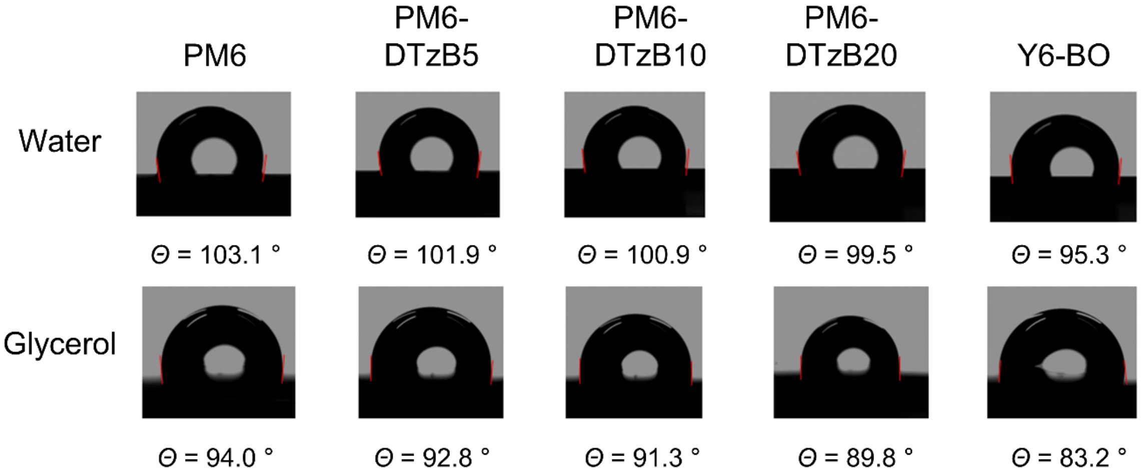


Fig. S14. Contact angle images of water and glycerol droplets on the neat P_Ds and Y6-BO SMA films.

Table S6. Contact angles of solvent droplets on the neat P_Ds and Y6-BO thin films and surface tension and corresponding interfacial tension between the P_D and Y6-BO SMA.

Material	Contact Angle [deg]		Surface Tension [mN m^{-1}]	$\gamma^{D\text{-}A}$ [mN m^{-1}]^{a}
	Water	Glycerol		
PM6	103.1	94.0	19.2	0.79
PM6-DTzB5	101.9	92.8	19.8	0.69
PM6-DTzB10	100.9	91.3	20.5	0.50
PM6-DTzB20	99.5	89.8	21.2	0.38
Y6-BO	95.3	83.2	24.8	-

[a)] The interfacial tension between the P_Ds and Y6-BO.

Table S7. RsoXS characteristics of P_D:Y6-BO blend films before and after annealing at 100 ^oC.

Blend	Annealing Time [h]	√TSI[a]	Domain Size [nm] [a]
PM6:Y6-BO	0	0.65	37
	72	1.00	43
PM6-DTzB10:Y6-BO	0	0.37	33
	72	0.40	32

[a] Estimated from the RSoXS profiles.

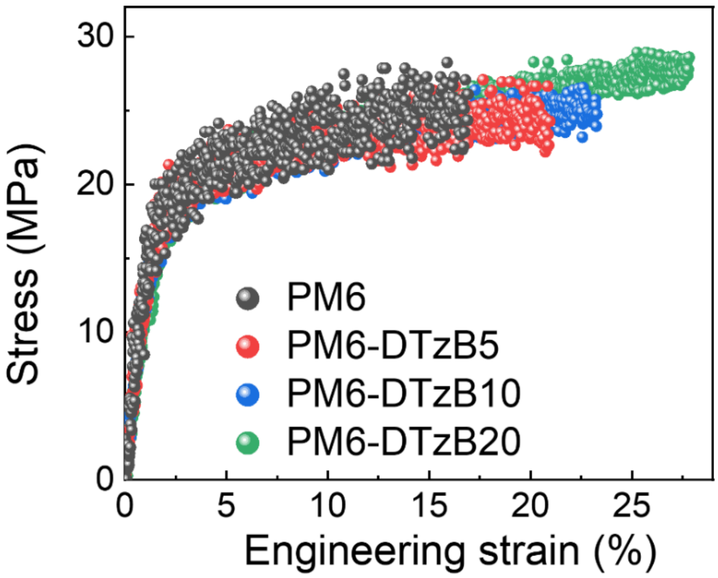


Fig. S15. Stress–strain curves of neat P_D films.

Table S8. Tensile properties of the neat P_D films.

Material	***E*[a]** **[GPa]**	**COS[a]** **[%]**	**Toughness[a]** **[MJ m^{-3}]**	**Thickness[a]** **[nm]**
PM6	0.7	16.9	3.7	98
PM6-DTzB5	0.8	20.7	4.6	89
PM6-DTzB10	0.8	23.1	5.1	92
PM6-DTzB20	0.8	28.0	6.5	95

[a] Average values were obtained from at least 3 different films.

Table S9. Tensile properties of the P_D:Y6-BO blend films.

Blend	***E***[a] **[GPa]**	**COS**[a] **[%]**	**Toughness**[a] **[MJ m^{-3}]**	**Thickness**[a] **[nm]**
PM6:Y6-BO	0.9	1.7	0.2	103
PM6-DTzB5:Y6-BO	1.0	5.5	1.0	95
PM6-DTzB10:Y6-BO	1.0	11.7	2.5	99
PM6-DTzB20:Y6-BO	1.0	17.0	3.7	93

[a] Average values were obtained from at least 3 different films.

References

1. Z. Wu, C. Sun, S. Dong, X.-F. Jiang, S. Wu, H. Wu, H.-L. Yip, F. Huang and Y. Cao, *J. Am. Chem. Soc.* 2016, **138**, 2004-2013.
2. J. Wang, C. Han, J. Han, F. Bi, X. Sun, S. Wen, C. Yang, C. Yang, X. Bao and J. Chu, *Adv. Energy Mater.*, 2022, **12**, 2201614.
3. J. Wang, C. Han, F. Bi, D. Huang, Y. Wu, Y. Li, S. Wen, L. Han, C. Yang, X. Bao and J. Chu, *Energy Environ. Sci.*, 2021, **14**, 5968-5978.