Supporting Information

Naphthalene-diimide-based all-conjugated block copolymer as an effective compatibilizer to improve the performance and thermal stability of all-polymer solar cells

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Experimental Section:

Synthesis of P1 (PNDT-2T)

The monomers A-Br_2 (0.126 mmol, 1.0 eq.) and D^1-Sn_2 (0.126 mmol, 1.0 eq.) were placed in a 50 mL two-necked flask purged with N_2 gas. After dissolving them in deoxidized toluene (35 mL), N_2 bubbling was conducted for 30 min. $Pd_2(dba)_3$ (13.7 mg, 0.0150 mmol) and P(*o*-tolyl)$_3$ (38.0 mg, 0.125 mmol) were added to start the polymerization and the solution was stirred at 110 °C for 24 h. Finally, 2-bromothiophene (0.0630 mmol, 0.50 eq.) and 2-tributylstannylthiophene (0.0315 mmol, 0.25 eq.) were added in the solution in this order and standing for 2 h and 2 h, respectively, for the end-capping treatment. The reaction was then quenched with a 5 M HCl solution (2 mL). The solution was extracted with chloroform and washed with water and KF (aq.), and it was purified *via* flash column chromatography (silica gel:K_2CO_3 = 9:1, w:w). The polymer solution was poured into MeOH (300 mL) to precipitate the polymer. The polymer was purified by Soxhlet extraction using hexane to remove the residual monomer and then extracted with chloroform. After distilling off the chloroform solution with an evaporator, a dark blue polymer was obtained, followed by freeze-drying from the benzene solution (0.135 g, 97 %). SEC: M_n = 26,100, M_w/M_n = 3.72. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 °C) d(ppm): 8.82 (s, 2H), 7.39 (s, 4H), 4.15-4.15 (m, 4H), 2.06-2.10 (m, 2H), 1.26-1.40 (m, 80H), 0.72-0.90 (m, 12H).

Synthesis of P2 (PNDI-DBDT)

The monomers A-Br_2 (0.126 mmol, 1.0 eq.) and D^2-Sn_2 (0.126 mmol, 1.0 eq.) were placed in a 50 mL two-necked flask purged with N_2 gas. After dissolving them in deoxidized toluene (35 mL), N_2 bubbling was conducted for 30 min. $Pd_2(dba)_3$ (13.7 mg, 0.0150 mmol) and P(*o*-tolyl)$_3$ (38.0 mg, 0.125 mmol) were added to start the polymerization and the solution was stirred at 110 °C for 24 h. Finally, 2-bromothiophene (0.0630 mmol, 0.50 eq.) and 2-tributylstannylthiophene (0.0315 mmol, 0.25 eq.) were added in the solution in this order and standing for 2 h and 2 h, respectively, for the end-capping treatment. The reaction was then quenched with a 5 M HCl solution (2 mL). The solution was extracted with chloroform and washed with water and KF (aq.), and it was purified *via* flash column chromatography (silica gel:K_2CO_3 = 9:1, w:w). The polymer solution was poured into MeOH (300 mL) to precipitate the polymer. The polymer was purified by Soxhlet extraction using hexane to remove the residual monomer and then extracted with chloroform. After distilling off the chloroform solution with an evaporator, a dark blue polymer was obtained, followed by freeze-drying from the benzene solution (0.132 g, 61 %). SEC: M_n = 20,400, M_w/M_n = 2.22. ^1H NMR (400 MHz, $C_2D_2Cl_4$, 80 °C) d(ppm) : 8.90 (s, 2H), 7.85 (s, 2H), 7.46 (s, 2H), 6.91 (s, 2H), 4.11-4.11 (m, 4H), 2.86-2.88 (m, 4H), 2.02-2.02 (m, 2H), 1.68-1.72 (m, 2H), 1.23-1.44 (m, 104H), 0.85-0.99 (m, 24H).

Table S1. Recent relevant progress of ternary BHJ all-PSCs.

Donor:Acceptor	Third component	PCE_{max} (%) ($PCE_{average}$)	Ref
PBDB-T:PNDI-2T-TR(5)	**J71 (10 wt%)**	9.12 (9.05)	32
PBDTTT-EF-T:N2200	**PCDTBT (10 wt%)**	6.65 (6.45)	33
PTB7-Th:NDP-V-C7	**PBCIT (15 wt%)**	9.03 (8.97)	34
PBDB-T:DCNBT-TPC	**PTB7-Th (40 wt%)**	12.1 (11.8)	35
PTB7-Th:N2200	**PBDD-ff4T (10 wt%)**	7.20 (6.90)	36

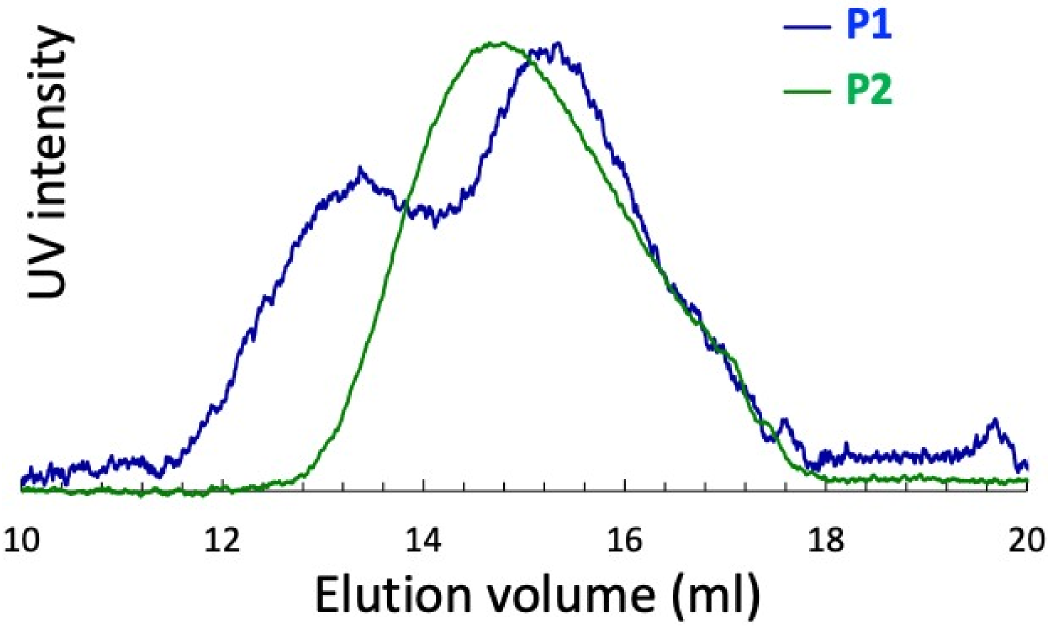

Fig. S1 SEC UV traces of P1 and P2.

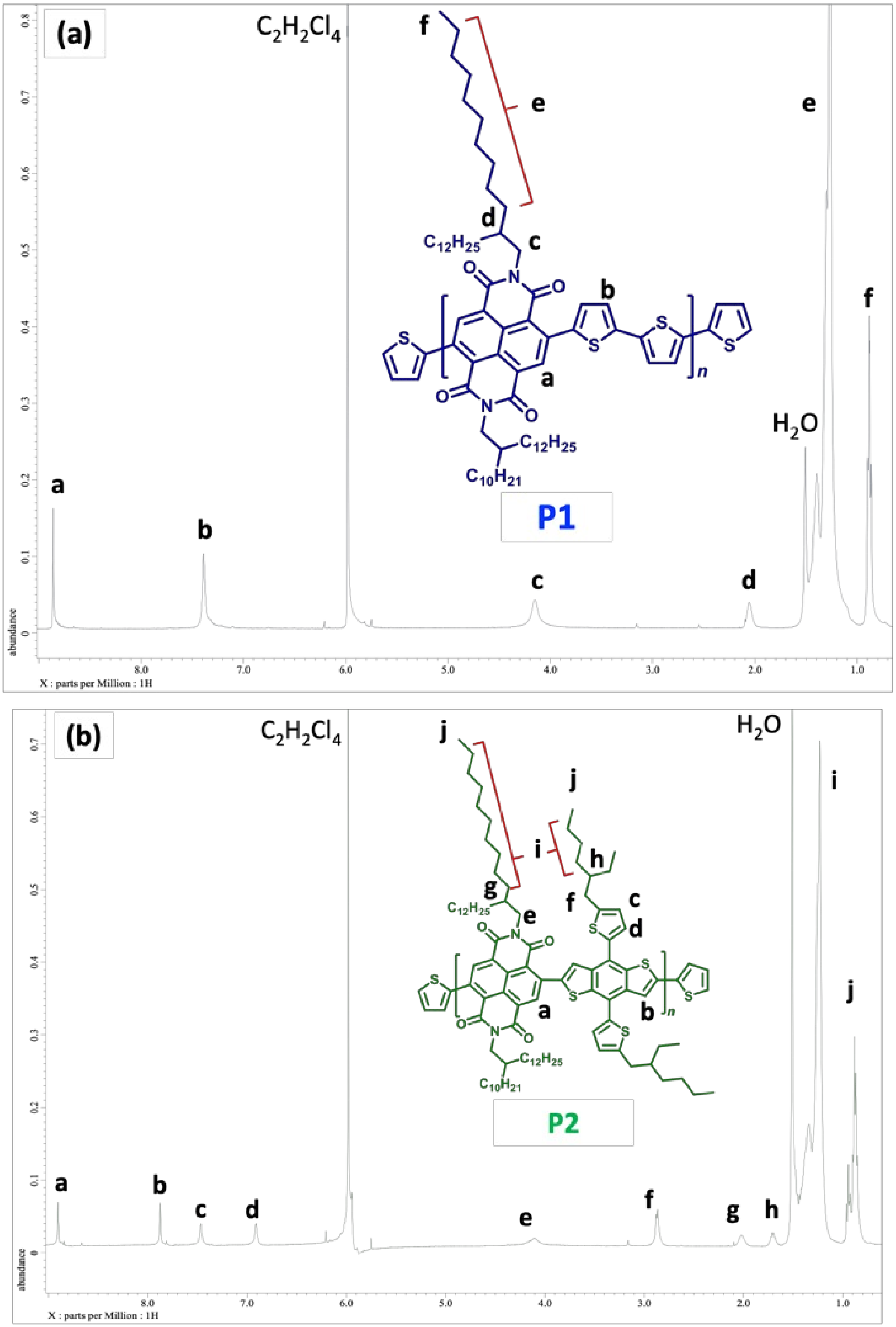

Fig. S2 ^{1}H NMR spectra of (a) P1 and (b) P2 in $C_2D_2Cl_4$ at 80 °C.

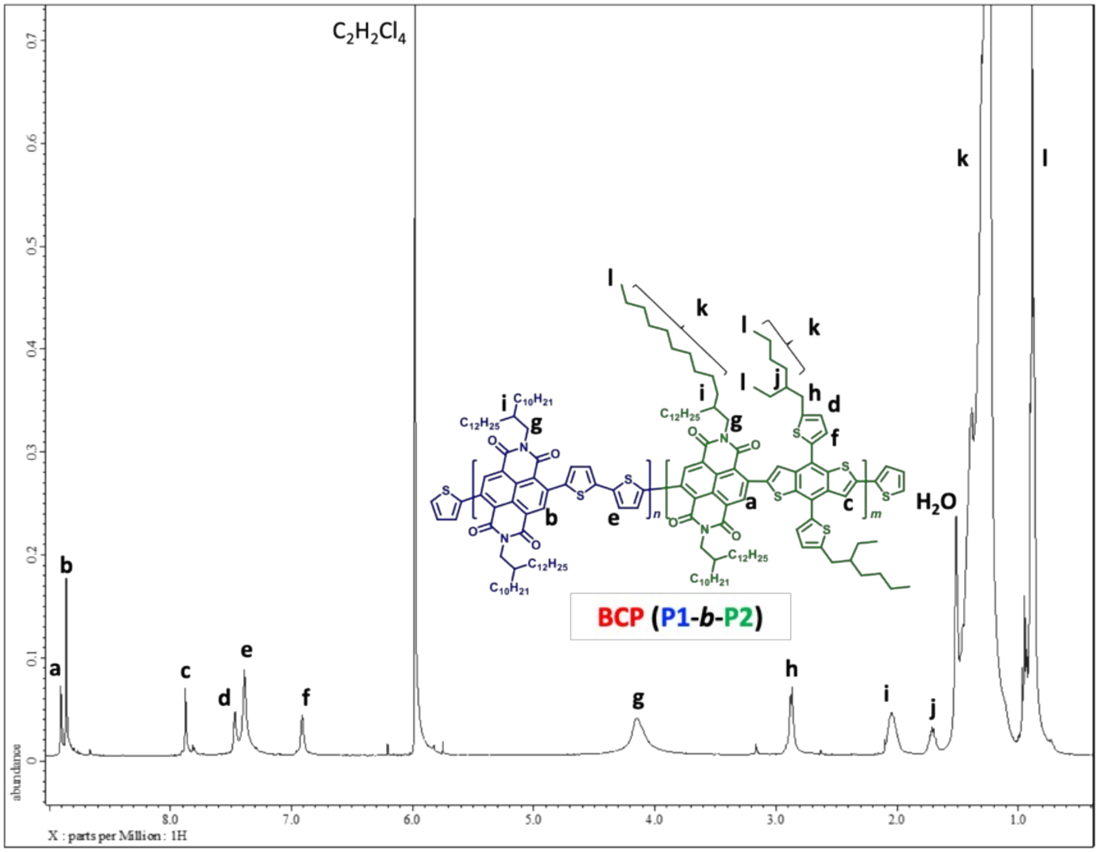

Fig. S3 ^{1}H NMR spectra of BCP in $C_2D_2Cl_4$ at 80 °C.

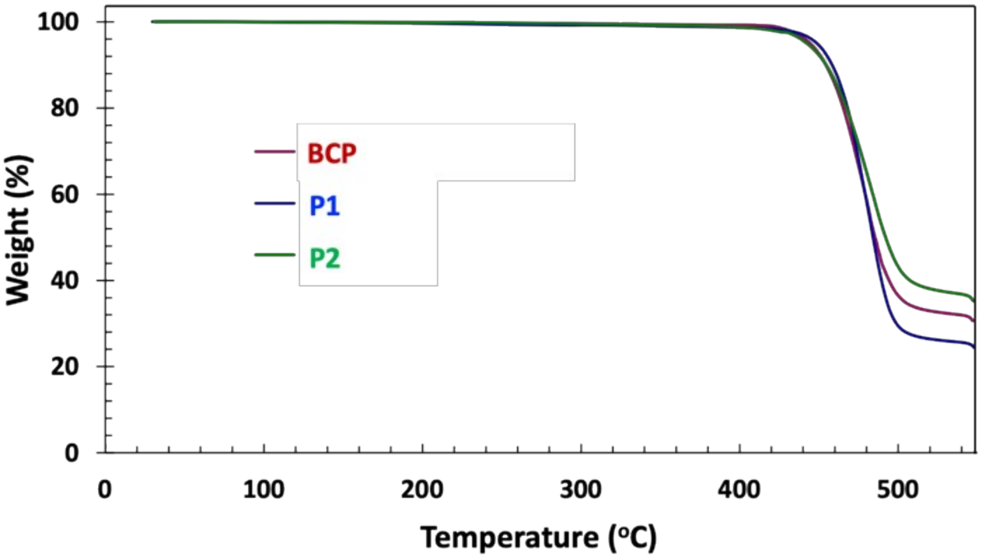

Fig. S4 TGA curves of BCP, P1, and P2.

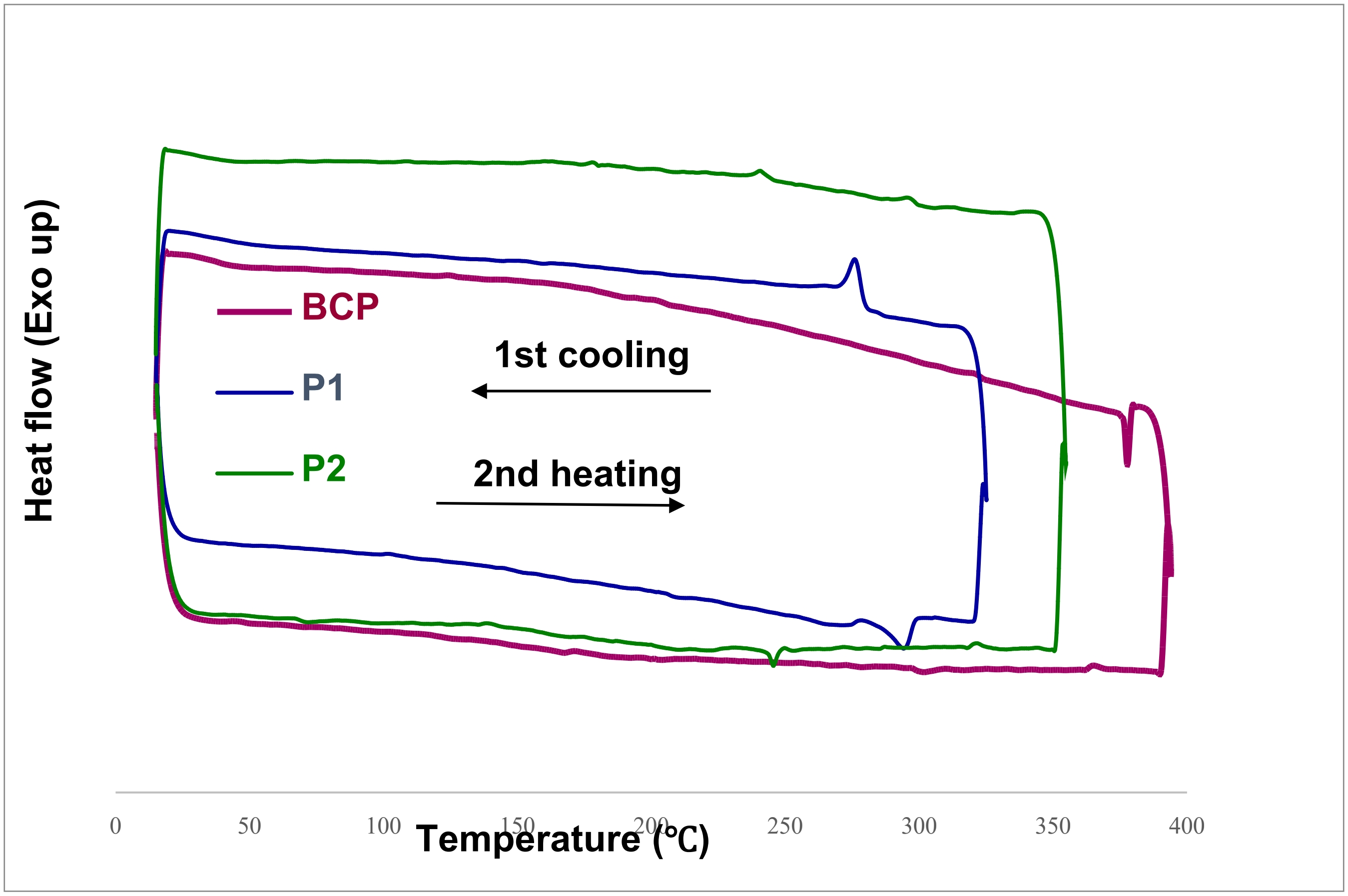

Fig. S5 DSC thermograms curves of BCP, P1, and P2.

Table S2. Thermal properties of P1, BCP, and P2.

	T_c (°C)	T_m (°C)
P1	276	290
BCP	—	—
P2	240	246

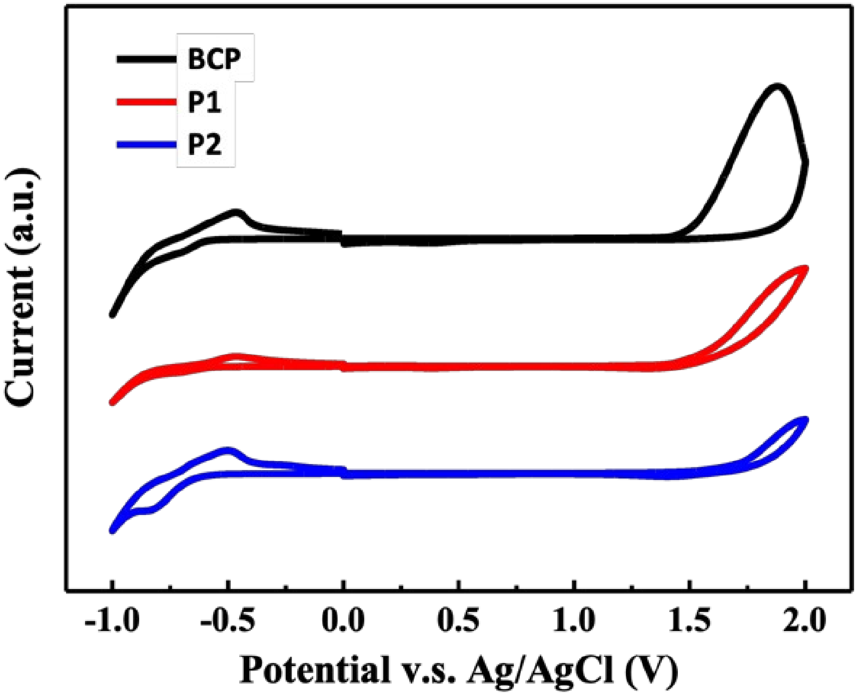

Fig. S6 CV curves of BCP, P1, and P2.

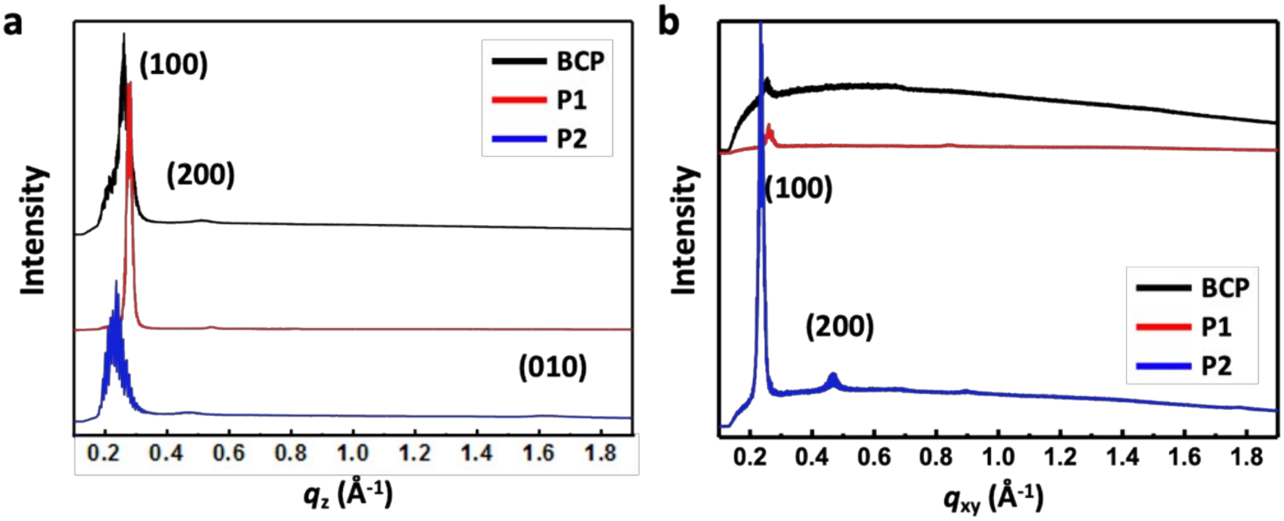

Fig. S7 1D-line-cutting profiles of the studied polymer films in the (a) out-of-plane direction and (b) in-plane direction, respectively.

Table S3. The crystallographic parameters and FET device parameters of the polymer films.

	μ_e (max/average) ($cm^2\ V^{-1}\ s^{-1}$)	I_{on}/I_{off}	V_{th} (V)	d_{lam} (Å)	In-plane FWHM ($Å^{-1}$)
P1	$2.9 \times 10^{-1} / 2.2 \times 10^{-1} \pm 5.0 \times 10^{-2}$	4×10^4	30	26.7	0.013
BCP	$1.7 \times 10^{-2} / 1.3 \times 10^{-2} \pm 3.0 \times 10^{-3}$	3×10^4	31	22.5	0.023
P2	$8.8 \times 10^{-4} / 7.3 \times 10^{-4} \pm 1.1 \times 10^{-4}$	3×10^3	26	24.0	0.017

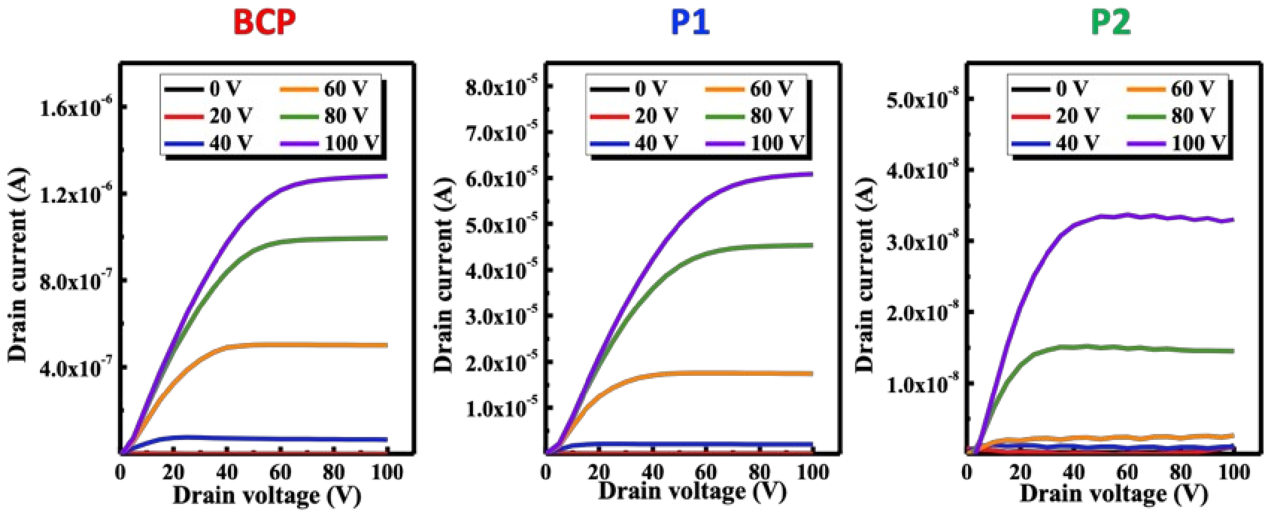

Fig. S8 Output characteristics of the FET devices based on the studied polymers.

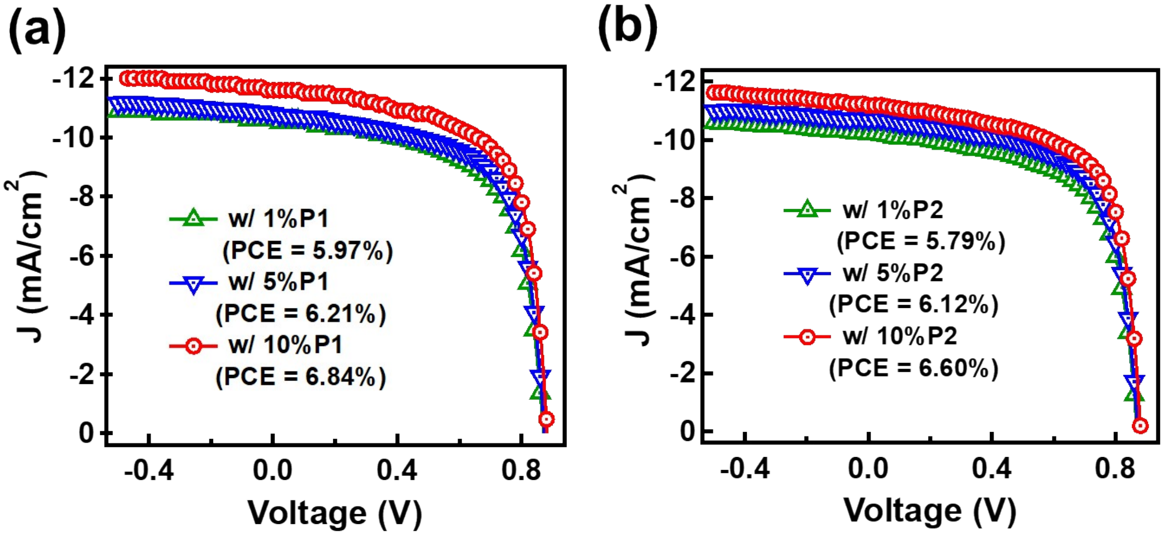

Fig. S9 The *J*-*V* curves of the (a) P1-based and (b) P2-based ternary BHJ device.

Table S4. Photovoltaic parameters of the fabricated OPV devices.

Compatibilizer	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE_{max} (%) ($\text{PCE}_{\text{average}}$)^b
1% P1[a]	0.870 (0.868±0.01)	10.56 (10.21±0.13)	65.0 (64.6±0.17)	5.97 (5.89±0.21)[b]
5% P1[a]	0.874 (0.870±0.01)	10.73 (10.46±0.18)	66.2 (65.7±0.14)	6.21 (6.16±0.16)[b]
10% P1[a]	0.883 (0.881±0.01)	11.65 (11.56±0.14)	66.5 (66.3±0.18)	6.84 (6.78±0.18)[b]
1% P2[a]	0.869 (0.867±0.01)	10.20 (10.14±0.21)	65.3 (64.9±0.17)	5.79 (5.75±0.19)[b]
5% P2[a]	0.872 (0.869±0.01)	10.70 (10.65±0.17)	65.6 (65.1±0.14)	6.12 (6.09±0.15)[b]
10% P2[a]	0.881 (0.879±0.01)	11.20 (11.16±0.15)	66.9 (66.5±0.13)	6.60 (6.54±0.13)[b]

[a] PBDB-T:N2200 BHJ system; [b] The average PCE shown in the parentheses are based on 15 devices.

Table S5. Surface energy of the thin films of P1, BCP, P2, and PBDB-T:N2200.

	θ_{water} (º)	$\theta_{glycerol}$ (º)	γ (mN/m)	x
PBDB-T:N2200	94.45	71.32	40.92	—
P1	99.91	76.67	36.41	0.132K
BCP	96.30	71.00	38.26	0.045K
P2	97.40	73.30	27.92	1.239K

Table S6. Fitting parameters of the GIWAXS profiles at the out-of-plane direction

Active layer	Compatibilizer	Peak (Å^{-1})	FWMH (Å^{-1})	q_z of PBDB-T of crystallite size (nm)
Fresh	None^{a}	20.4	0.064	8.83
	1% BCP^{a}	19.9	0.075	7.54
Thermal-stress	None^{a}	20.3	0.050	11.3
	1% BCP^{a}	19.9	0.073	7.64

[a] PBDB-T:N2200 BHJ system