

Supplementary Information

Polymer Solar Cells made with Photocrosslinkable Conjugated Donor-Acceptor Block Copolymers: Improvement in the Thermal Stability and Morphology with a Single-Component Active Layer

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Characterization and measurements

Instrumentation

The structures of all the synthesized compounds were analyzed using ^1H NMR spectroscopy using a Bruker 500 MHz spectrometer (Ascend 500). The molecular weight characteristics, such as M_n and PDI, of the polymers were determined relative to polystyrene standards *via* gel permeation chromatography (GPC; Agilent GPC 1200 series) using 1,2-dichlorobenzene (ODCB). The masses of the synthesized compounds were determined using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF/TOF™ 5800, AB SCIEX) at the Korea Basic Science Institute (Seoul). The absorption spectra of the polymers in chloroform solutions and thin films were recorded using a UV-vis absorption spectrometer (Agilent 8453, photodiode array, $\lambda = 190\text{--}1100$ nm). The oxidation and reduction potentials of the polymers were measured *via* cyclic voltammetry. Thin films were coated onto a Pt sheet using chloroform. The electrolyte solution used was 0.10 M tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) in freshly dried acetonitrile. Ag/AgCl (diameter = 0.5 mm) electrodes were used as the reference and counter electrodes.

PSC fabrication and characterization

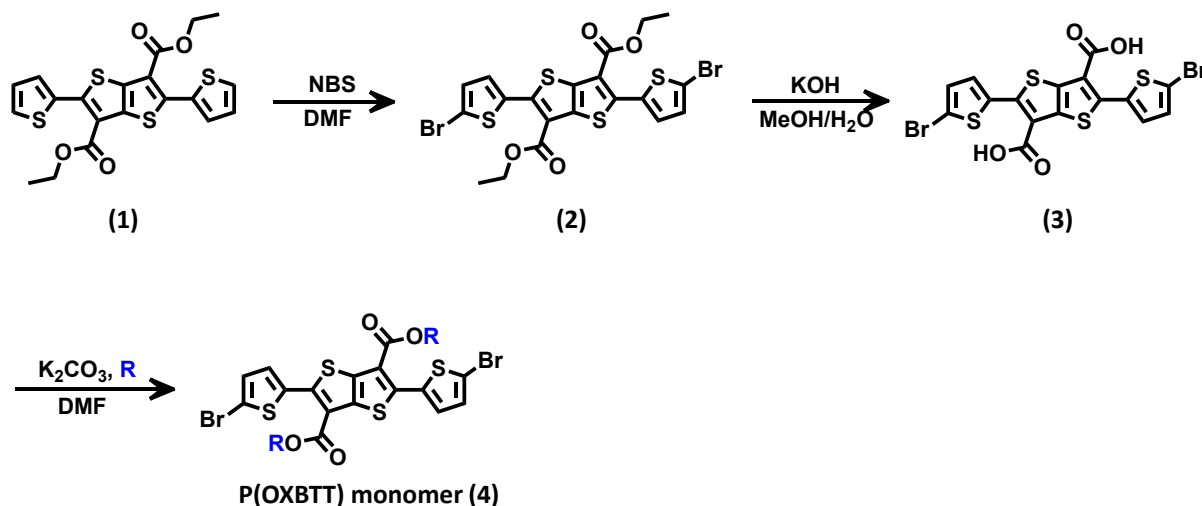
The inverted all-PSCs were fabricated according to the following device configuration: ITO (150 nm)/ZnO (30 nm)/active layer (80–100 nm)/ MoO_3 (10 nm)/Ag (100 nm). The ZnO layer was spin-coated for 40 s at 3000 rpm onto the ITO glass, which was pretreated for 20 min with UV-ozone. Then, the ZnO thin film was annealed at 165 °C for 1 h. Subsequently, the substrate was transferred to an N_2 -protected glove box. Next, the active layer of the PSC was spin-coated onto the ZnO layer using a 2.0 wt.% chlorobenzene solution. After stirring the combined solution overnight at 60 °C, it was spin-coated onto the ITO/ZnO substrate at 3000 rpm for 40

s. Finally, MoO₃ (10 nm) and Ag (100 nm) were deposited onto the active layer *via* vacuum thermal evaporation. The *J-V* characteristics of the fabricated PSCs were measured using a Keithley 2400 source meter at 100 mW cm⁻² (Oriel, 1000 W) under AM 1.5 G illumination. The EQE spectra of the PSCs were recorded using a K3100 EQX instrument equipped with a K240 XE300 lamp.

Experimental section

Materials

All chemicals used for the synthesis of **P(OXBTT)**, **P(NDI2T)**, and **P(OXBTT-co-NDI2T)** were purchased from Sigma-Aldrich and Across Organics and used as received without further purification. The reagent-grade solvents (e.g., toluene) used in this study were purified using standard distillation methods. Compounds **(1)** and **P(NDI2T)** copolymer were synthesized according to a previously reported procedure.^{S1-3}



Scheme S1. Synthesis of **P(OXBTT)** monomer.

Diethyl 2,5-bis(5-bromothiophen-2-yl)thieno[3,2-b]thiophene-3,6-dicarboxylate (2)

Compound (1) (600 mg, 1.33 mmol) and NBS (626 mg, 5.35 mmol) were poured into a round-bottom flask with DMF (20 mL), and the mixture was stirred at room temperature for 12 h.

After the reaction completion, the mixture was filtered and rinsed with water. The crude product was purified by silica-gel column chromatography (CH₂Cl₂:n-hexane = 1:1 v/v) and then filtered from methanol to collect the yellow solid powder with a yield of 32% (560 mg). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.35 (d, *J*=3.97 Hz, 2 H) 7.07 - 7.09 (m, 2 H) 4.33 (q, *J*=7.12 Hz, 4 H) 1.30 (t, *J*=7.17 Hz, 6 H).

2,5-Bis(5-bromothiophen-2-yl)thieno[3,2-b]thiophene-3,6-dicarboxylic acid (3)

Compound (2) (400 mg, 0.66 mmol) and KOH (110 mg, 2.0 mmol) were placed in a round-bottomed flask with water (5 mL) and MeOH (20 mL). The mixture was stirred overnight at 60 °C. After the reaction was complete, the mixture was acidified using aqueous HCl. The crude product was then filtered and rinsed with water. The residue (350 mg, 96% yield) was used in the subsequent reaction without further purification.

Bis(6-((3-methyloxetan-3-yl)methoxy)hexyl) 2,5-bis(5-bromothiophen-2-yl)thieno[3,2-b]thiophene-3,6-dicarboxylate (4, P(OXBTT) monomer)

Compound (3) (200 mg, 0.36 mmol) and K₂CO₃ (150 mg, 1.08 mmol) were added to a round-bottom flask with DMF (20 mL), and the mixture was stirred at 60 °C for 20 min. 3-(((6-bromohexyl)oxy)methyl)-3-methyloxetane (240 mg, 0.90 mmol) was added in one portion, and the mixture was stirred overnight at 60 °C. After the reaction completion, the mixture was filtered and rinsed with water. The powder was dried under anhydrous MC and Na₂SO₄ and filtered. The crude product was purified by silica-gel column chromatography (CH₂Cl₂:n-hexane = 1:1 v/v) and then filtered from methanol to collect the light-yellow solid powder with a 45% yield (150 mg). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.31 (d, *J*=3.97 Hz, 2 H) 7.08 (d, *J*=3.97 Hz, 2 H) 4.50 (d, *J*=5.80 Hz, 4 H) 4.34 - 4.38 (m, 8 H) 3.45 - 3.49 (m, 8 H) 1.80 (m, 4

H) 1.62 (m, 4 H) 1.41 - 1.47 (m, 8 H) 1.30 (s, 6 H). ^{13}C NMR (125 MHz, CDCl_3) δ ppm 145.46, 137.01, 135.27, 130.01, 129.97, 119.80, 116.27, 80.22, 76.11, 71.44, 65.66, 39.91, 29.49, 28.58, 25.89, 25.83, 21.39. MALDI-TOF: m/z 918.05 $[\text{M}]^+$.

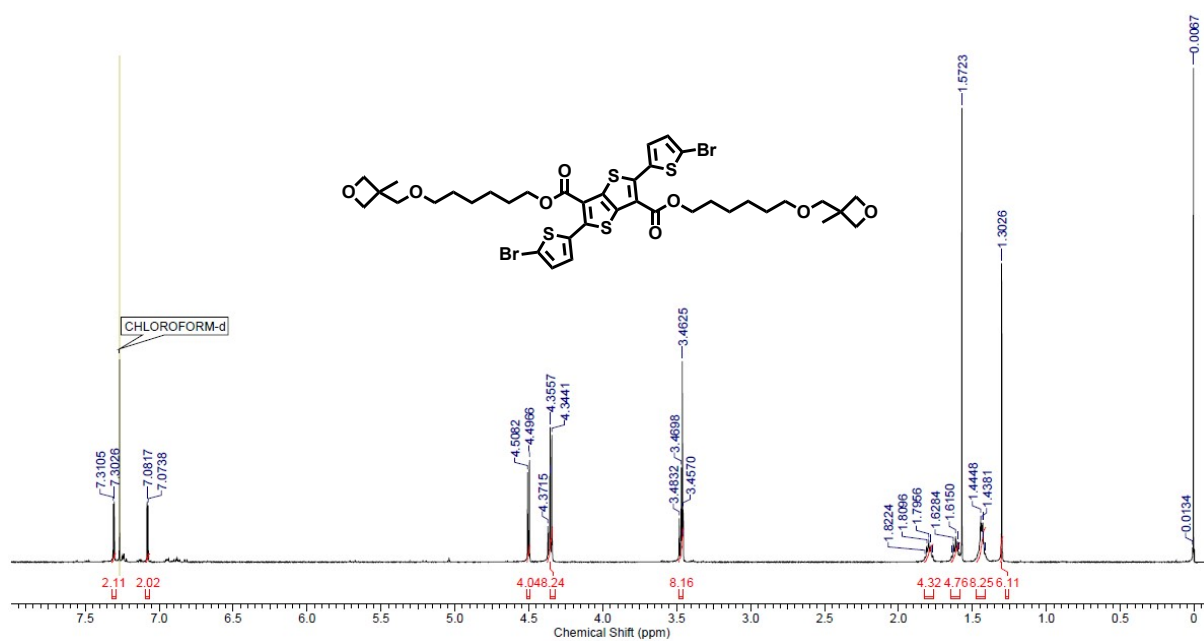


Fig. S1. ^1H NMR spectra of P(OXBTT) monomer.

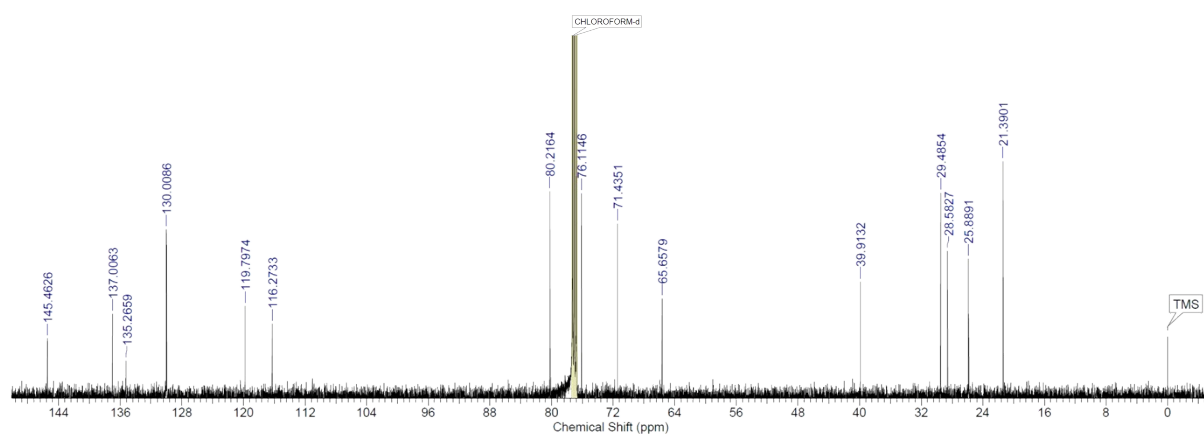


Fig. S2. ^{13}C NMR spectra of P(OXBTT) monomer.

Polymerization of P(OXBTT)

To obtain the **P(OXBTT)** polymer, M3 (100 mg, 0.11 mmol, 1 eq.), M4 (101 mg, 0.11 mmol, 1 eq.), and Pd(PPh₃)₄ were added to a Schlenk tube. Dry toluene (4.5 mL) and DMF (0.5 mL) were added, and the mixture was degassed. The reactor was stirred and refluxed for 10 h at 110 °C. After cooling to room temperature, the resulting solution was precipitated in methanol (300 mL). The byproducts, namely the unreacted monomer and oligomers, were removed using successive Soxhlet extractions with acetone and n-hexane. The concentrated MC fraction was then precipitated in methanol (300 mL) and dried under a vacuum at 60 °C for 24 h GPC: $M_n = 35.0 \text{ kg mol}^{-1}$; $M_w = 91.4 \text{ kg mol}^{-1}$; PDI = 2.60).

Polymerization of P(OXBTT-co-NDI2T)

To prepare the **P(NDI2T)** monomer, M1 (108 mg, 0.11 mmol, 1 eq.), M2 (55 mg, 0.11 mmol, 1 eq.), and Pd(PPh₃)₄ were dissolved in toluene (5 mL), and the reaction mixture was degassed. The temperature was gradually increased to 110 °C while stirring the reaction mixture. After 7 h, the mixed toluene solution (3 mL) of M3 (100 mg, 0.11 mmol, 1 eq.) and M4 (101 mg, 0.11 mmol, 1 eq.) was added to the reactor, in which **P(NDI2T)** was prepared. The reaction mixture was kept under stirring at 110 °C for 48 h. The resulting solution was cooled and precipitated in methanol (300 mL). The byproducts and residual oligomers were eliminated by Soxhlet extraction with acetone and hexane. The MC fraction was then poured into methanol (300 mL) and the precipitated products were dried in vacuo at 60 °C for 24 h. GPC: M_n of 29.1 kg mol⁻¹; M_w of 74.3 kg mol⁻¹; PDI of 2.55). Elemental Anal. Found for (C₇₂H₈₆O₈S₈)_m-(C₇₀H₁₀₄N₂O₄S₂)_n: C, 70.62; H, 7.89; N, 1.38; S, 13.46; m:n ≈ 1:1.

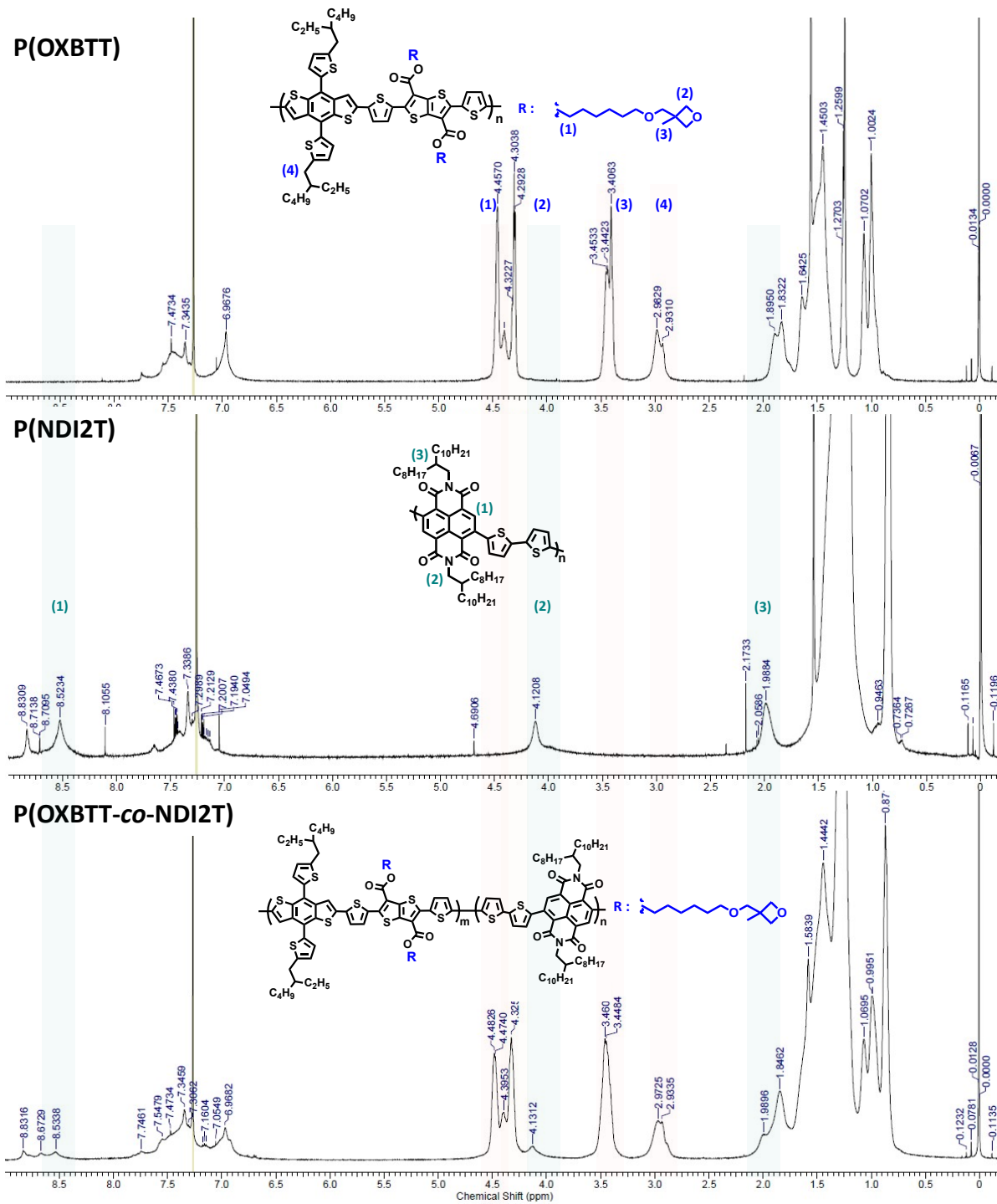
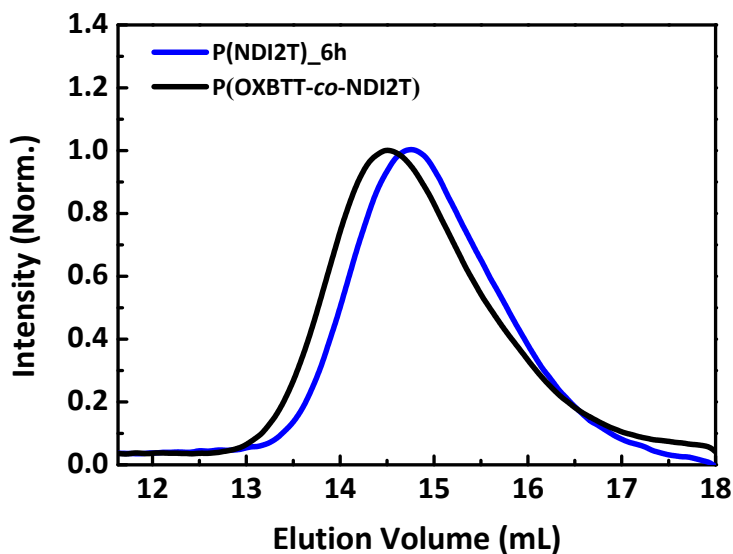


Fig. S3. ^1H NMR spectra of P(OXBTT), P(NDI2T), and P(OXBTT-co-NDI2T).



Polymer	M_n (kg mol ⁻¹)	M_w (kg mol ⁻¹)	PDI
P(NDI2T)	23.7	55.1	2.32
P(OXBTT-co-NDI2T)	29.1	74.3	2.55

Fig. S4. Number average molecular weight (M_n) and polydispersity index (PDI) data obtained from gel permeation chromatography of P(OXBTT-co-NDI2T).

Table S1. Elemental analysis results for polymers.

Polymer	Formula		C%	H%	N%	S%
P(OXBTT)	$(C_{72}H_{86}O_8S_8)_n$	Calc.	64.73	6.49	0	19.20
		Found	66.15	6.63	0	19.04
P(NDI2T)	$(C_{62}H_{88}N_2O_4S_2)_n$	Calc.	75.26	8.96	2.83	6.48
		Found	75.25	8.96	2.84	6.47
P(OXBTT-co-NDI2T)	$(C_{72}H_{86}O_8S_8)_m-$ $(C_{62}H_{88}N_2O_4S_2)_n$	Calc. (m:n =1:1)	69.99	7.72	1.41	12.84
		Found	70.62	7.89	1.38	13.46

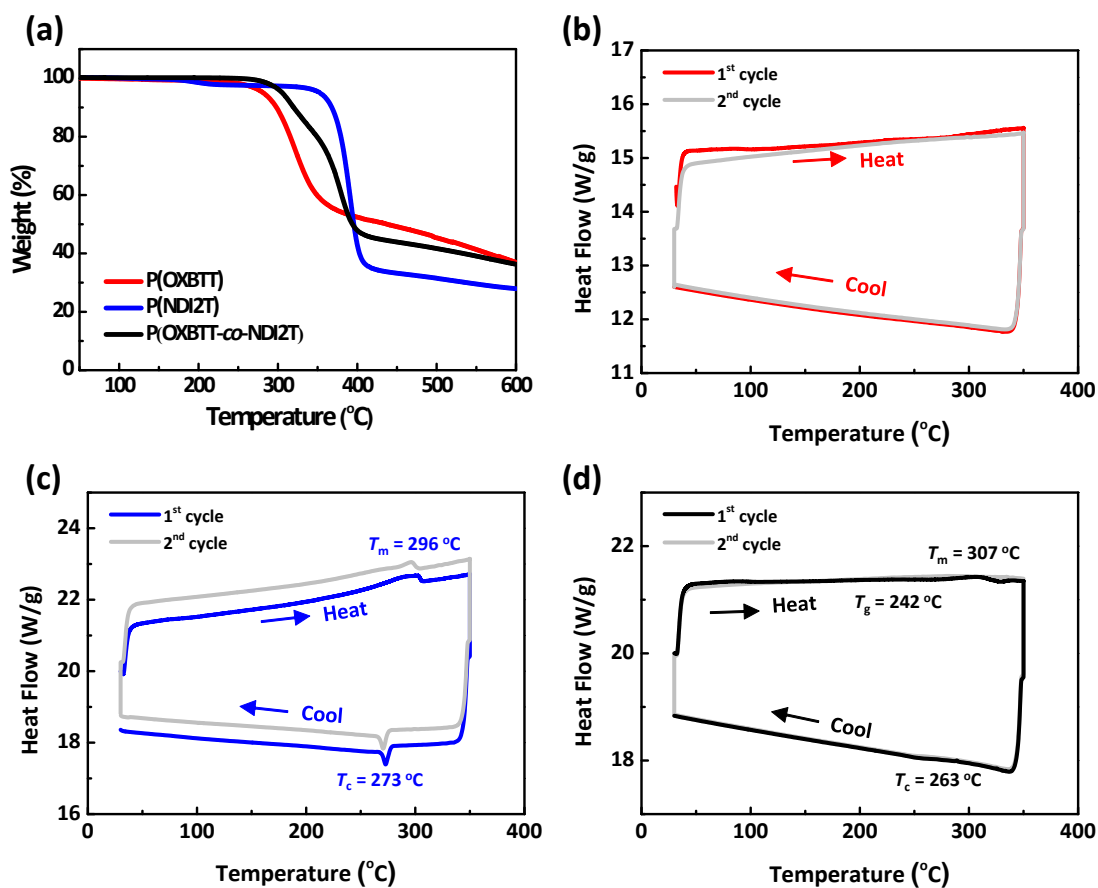


Fig. S5. (a) TGA curve and DSC thermograms of (b) P(OXBTT), (c) P(NDI2T), and (d) P(OXBTT-co-NDI2T) measured at a scan rate of 10 °C per minute.

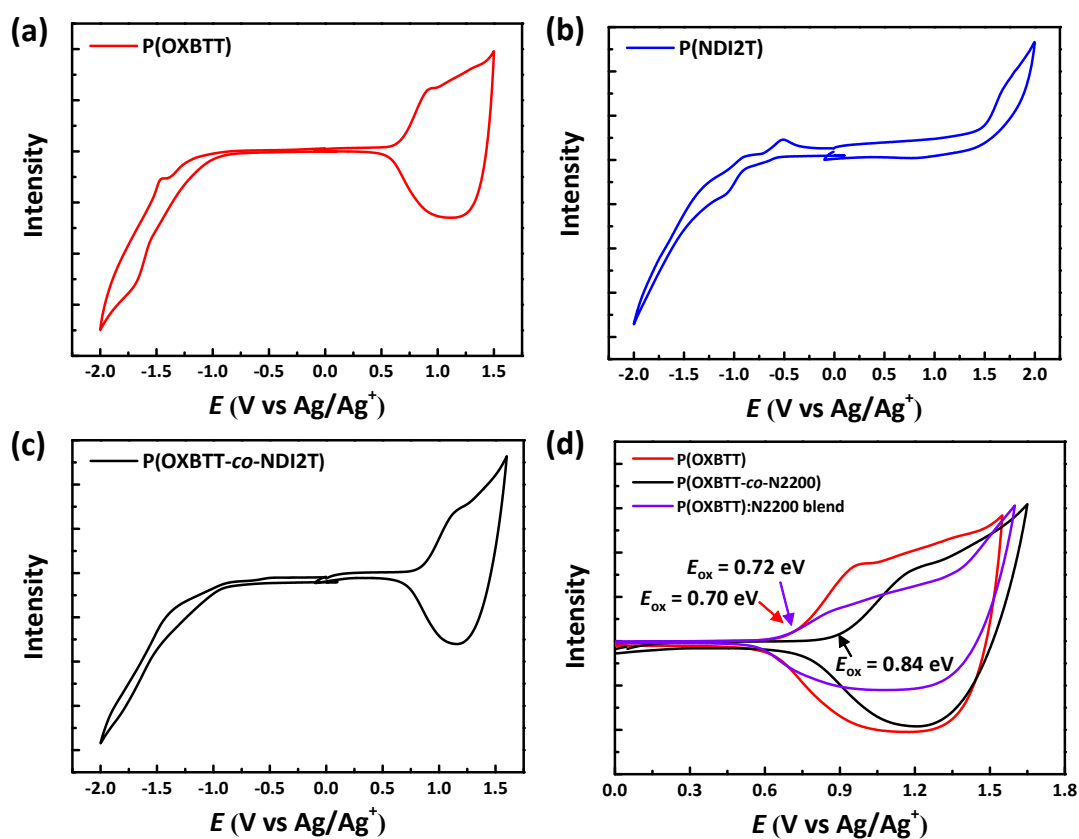


Fig. S6. Cyclic voltammograms of (a) P(OXBTT), (b) P(NDI2T), (c) P(OXBTT-co-NDI2T), and (d) blend(P(OXBTT):P(NDI2T)=1:1).

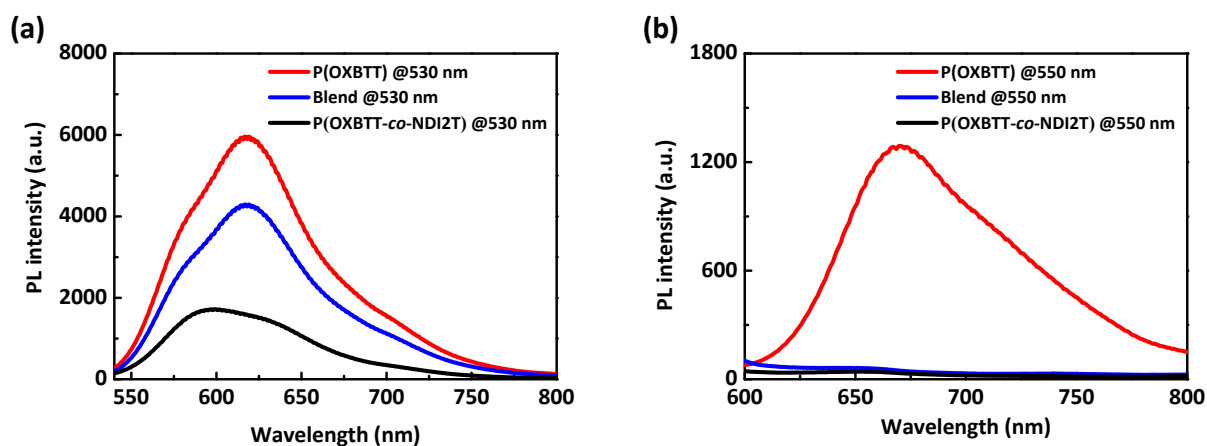


Fig. S7. (a,b) Photoluminescence spectra of P(OXBTT), blend, and P(OXBTT-co-NDI2T) in (a) solution (excited at 530 nm) and (b) film states (excited at 550 nm).

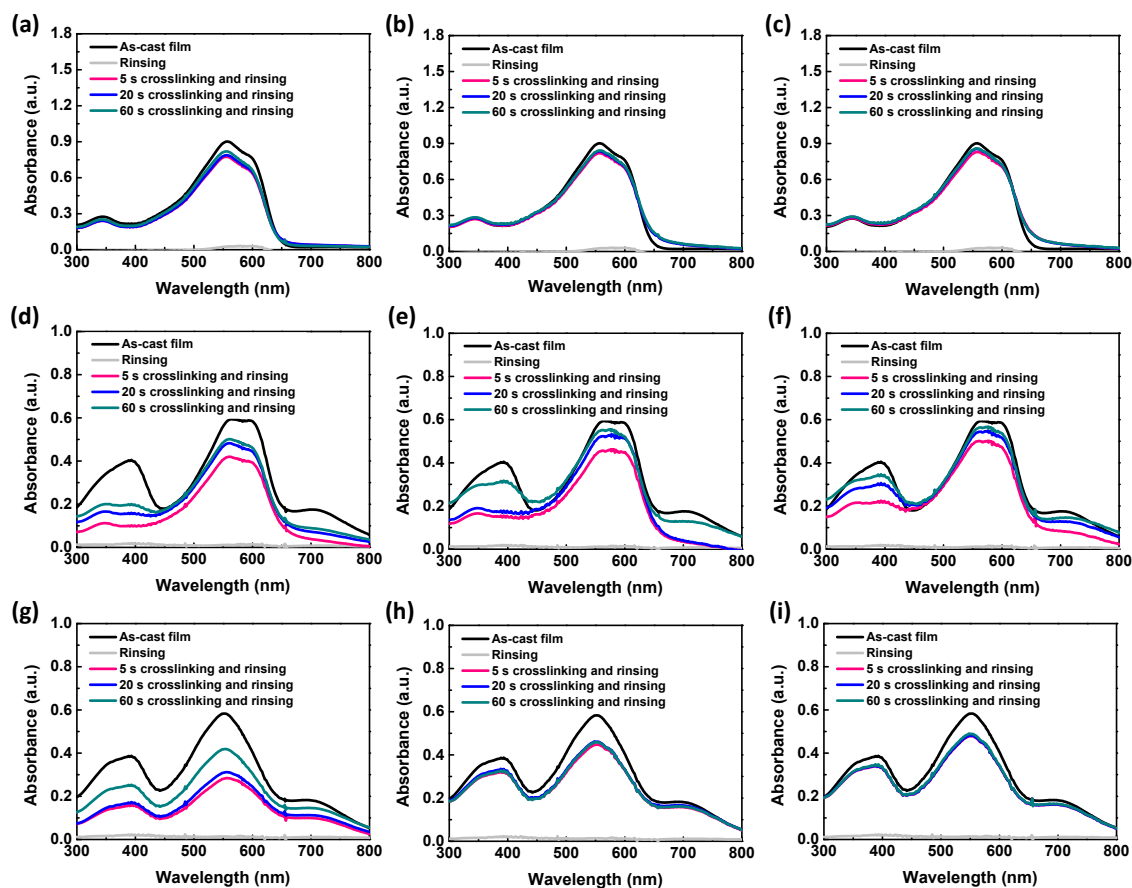


Fig. S8. UV-vis absorption spectra of (a, b, c) **P(OXBTT)**, (d, e, f) **blend**, (g, h, i) **P(OXBTT-co-NDI2T)** films. The spectra obtained from the crosslinked film (a, d, g) 1.0 wt% PAG, 150 °C, (b, e, h) 2.0 wt% PAG, 150 °C, (c, f, i) 2.0 wt% PAG, 180 °C during difference irradiation time after rinsing with ODCB.

Table S2. Crosslinking % of the polymer films.

Material	UV irradiation time	Crosslinking condition		
		PAG 1.0 wt% 150 °C	PAG 2.0 wt% 150 °C	PAG 2.0 wt% 180 °C
P(OXBTT)	5 s	86.02	90.91	91.87
	20 s	87.46	92.64	94.77
	60 s	90.91	93.28	95.30
Blend	5 s	70.46	76.75	84.14
	20 s	81.00	88.10	91.16
	60 s	84.21	92.86	94.97
P(OXBTT-co-NDI2T)	5 s	48.83	76.85	82.08
	20 s	53.59	78.72	82.41
	60 s	71.97	79.16	83.82

* The crosslinking % was calculated at 555 nm. Non-crosslinked film Almost 98% washed away.

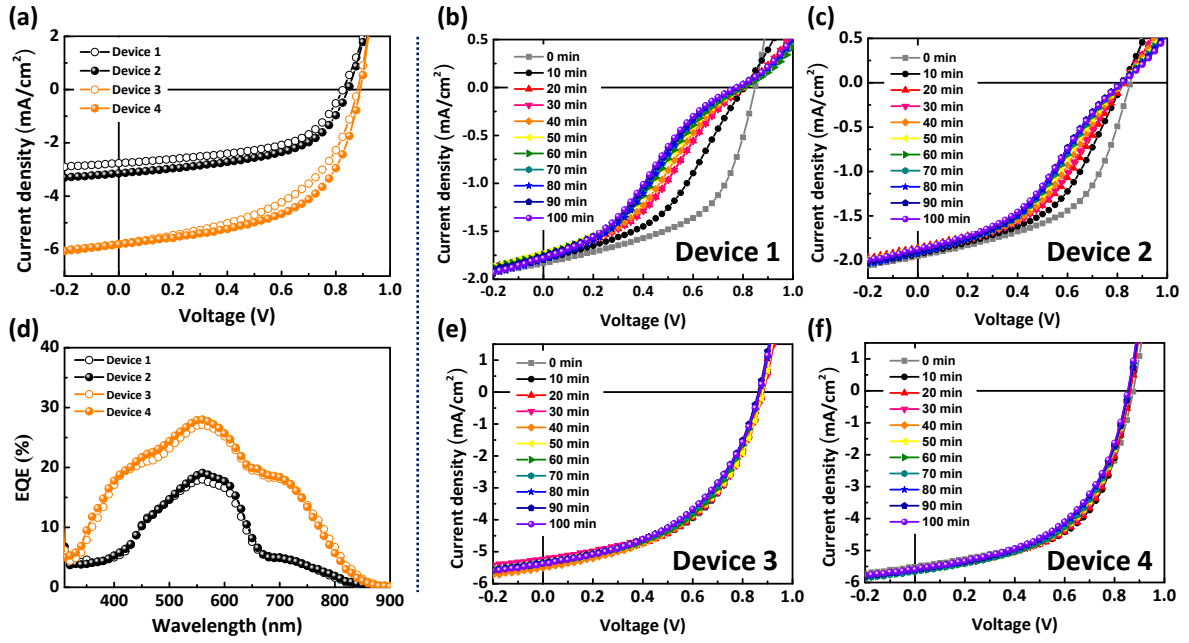


Fig. S9. (a) J - V characteristics, (d) EQE spectra of PSCs with a photoactive layer of **P(OXBTT):P(NDI2T)** blend (1:1 wt. ratio) and **P(OXBTT-co-NDI2T)** films. (b,c,e,f) J - V curves after thermal aging at 80 °C in ambient conditions. (Device 1: As-cast blend film, device 2: UV irradiated blend film, Device 3: as-cast **P(OXBTT-co-NDI2T)** film, and device 4: UV irradiated **P(OXBTT-co-NDI2T)** film)

Table S3. Photovoltaic performance of PSCs with a device structure of ITO/ZnO/Active layer/MoO₃/Ag under AM 1.5G illumination (100 mW cm⁻²).

Device	Active layer	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	PCE [%]	R_s [Ω cm ²]	R_{SH} [Ω cm ²]
1	P(OXBTT):P(NDI2T)	0.82	3.07	0.54	1.36	47.01	1389.07
2		0.84	3.13	0.53	1.47	40.93	1184.36
3	P(OXBTT-co-NDI2T)	0.87	5.78	0.50	2.55	24.51	678.61
4		0.88	5.80	0.56	2.89	18.92	811.34

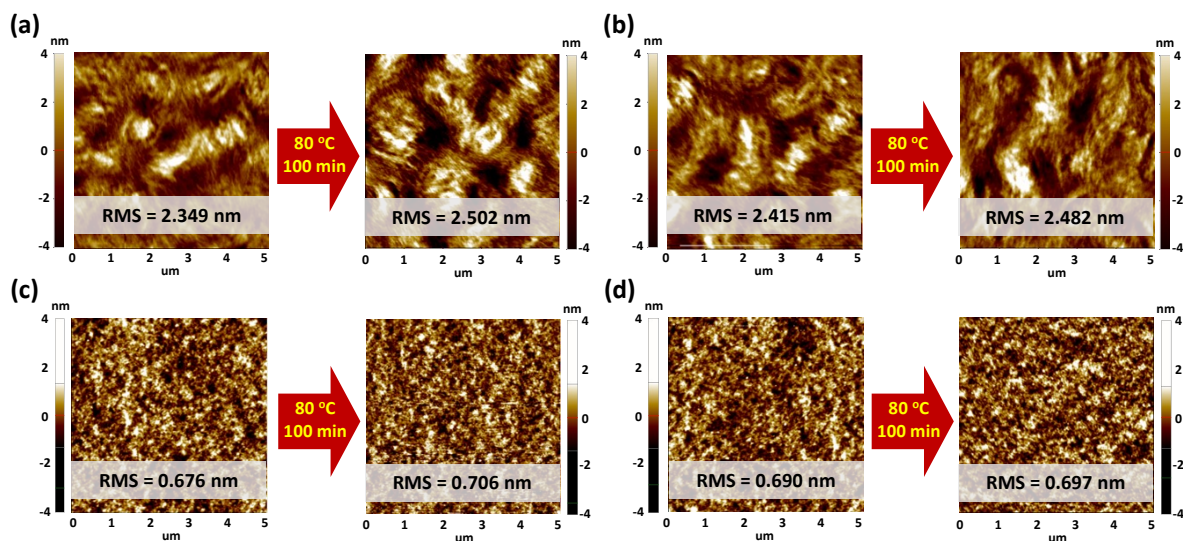


Fig. S10. AFM height images of the photoactive layer of **P(OXBTT):P(NDI2T)** blend (1:1 wt. ratio) and **P(OXBTT-co-NDI2T)** films before (left) and after thermal aging (right) at 80 °C for 100 min. (a) Device 1: As-cast blend film, (b) device 2: UV irradiated blend film, (c) device 3: as-cast **P(OXBTT-co-NDI2T)** film, and (d) device 4: UV irradiated **P(OXBTT-co-NDI2T)** film.

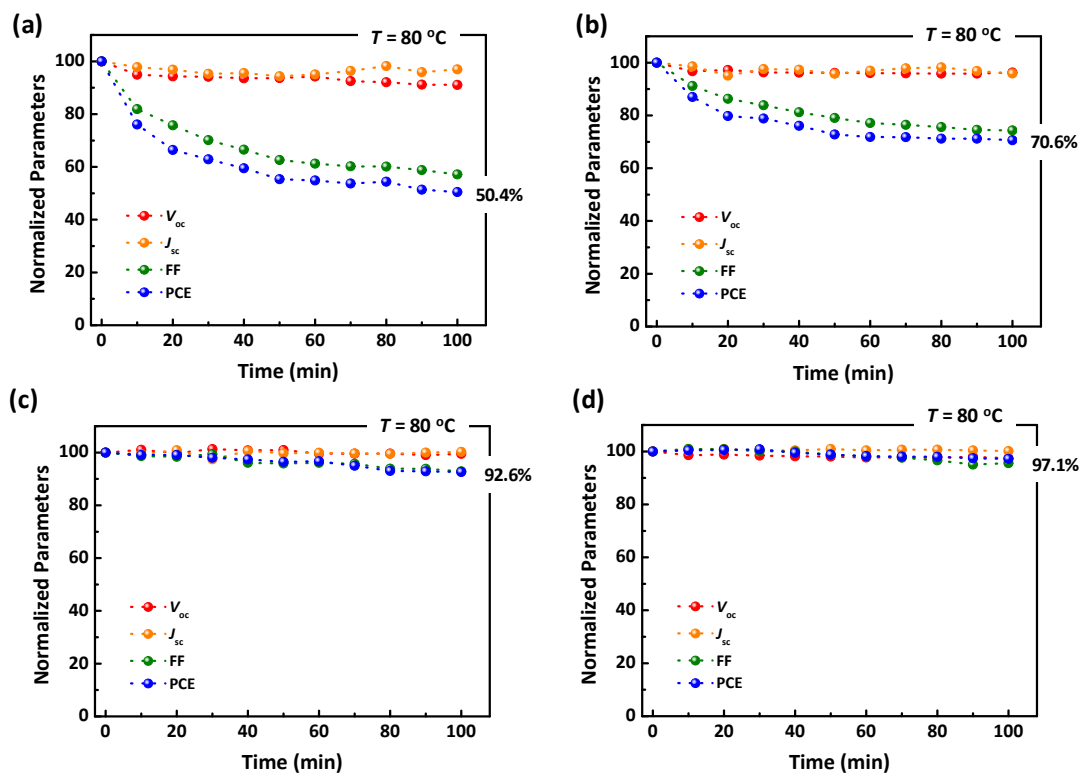


Fig. S11. Normalization parameters of the PSC performance in ambient conditions after thermal aging at 80 °C for 100 min. (a) As-cast blend film, (b) UV irradiated blend film, (c) as-cast **P(OXBTT-co-NDI2T)** film, and (d) UV irradiated **P(OXBTT-co-NDI2T)** film.

References

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S3. N. Y. Kwon, S. H. Park, H. Kang, A. V. Takaloo, A. K. Harit, H. Y. Woo, T. G. Kim, H. J. Yoon, M. J. Cho and D. H. Choi, *J. Mater. Chem. A*, 2020, **8**, 20091-20100.