

# Supplementary Information for

## Effects of Conjugation Spacers in Diketopyrrolopyrrole-Based Copolymers for All-Polymer-Based Photodiodes

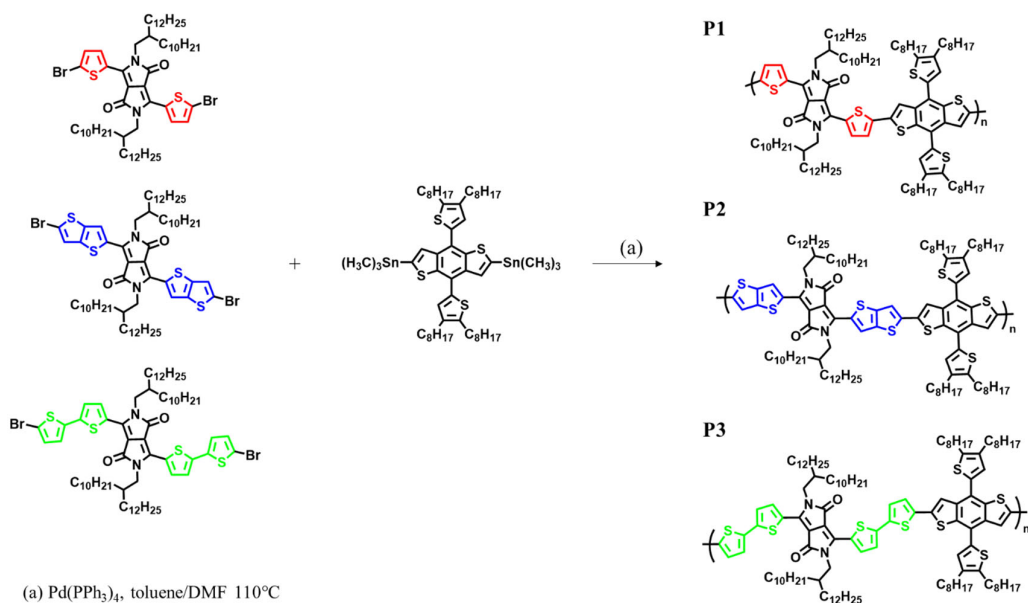
Hyunbum Kang <sup>1,†</sup>, Hyungjun Kim <sup>1,†</sup>, Ajeong Choi <sup>1</sup>, Youngjun Yun <sup>2,\*</sup> and Gaehwang Lee <sup>1,\*</sup>

<sup>1</sup> Material Research Center, Samsung Advanced Institute of Technology (SAIT), Samsung Electronics, Suwon 16678, Republic of Korea

<sup>2</sup> School of Semiconductor Display Technology, Hallym University, Chuncheon 24252, Republic of Korea

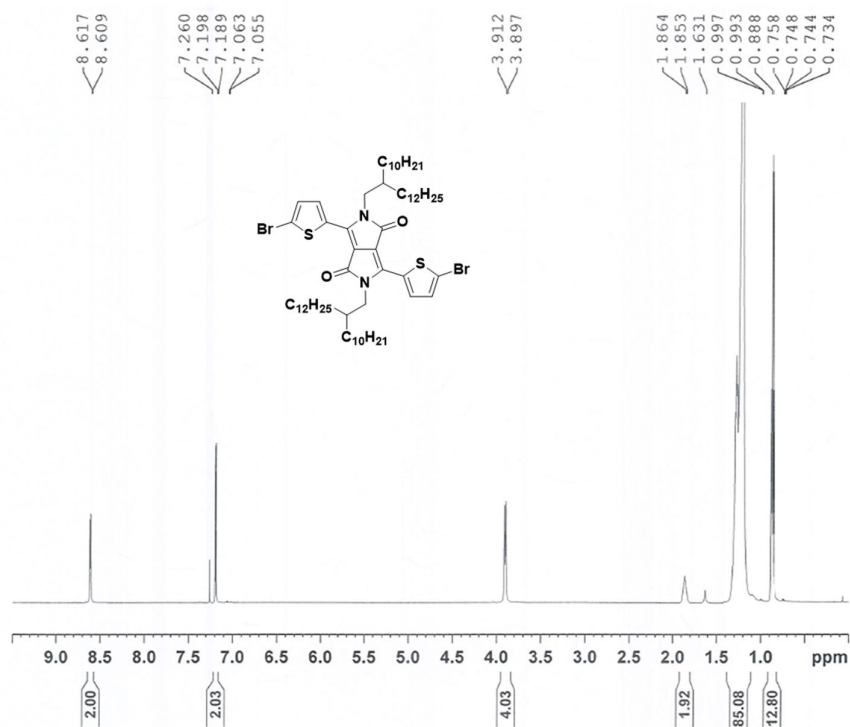
\* Correspondence: youngjun.yun@hallym.ac.kr (Y.Y.); gaehwang.lee@samsung.com (G.H.L.)

† These authors contributed equally to this work.

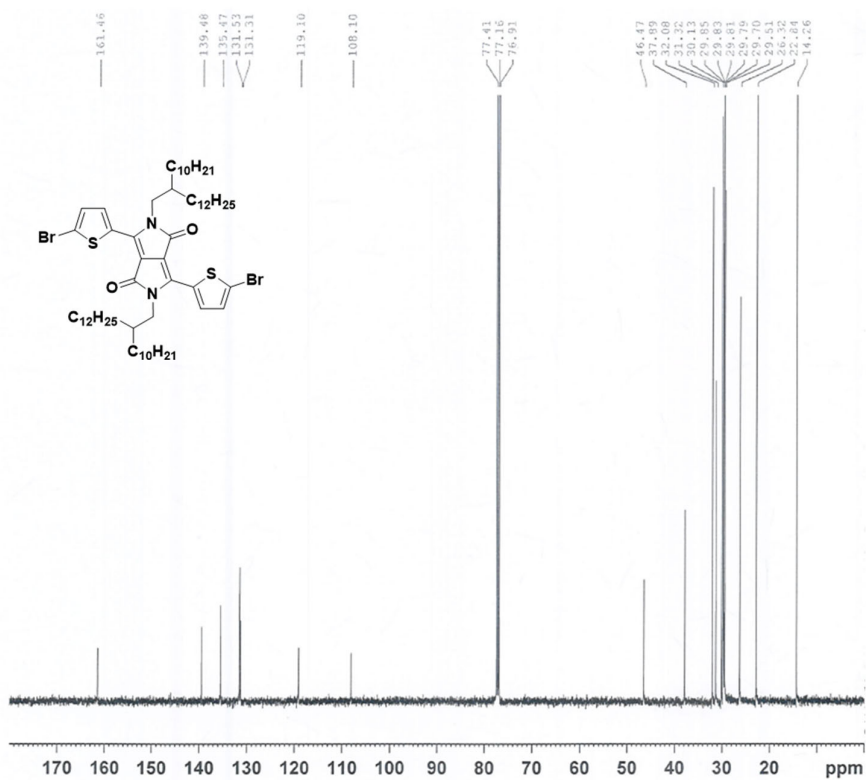


**Figure S1.** Synthetic procedures for P1, P2 and P3

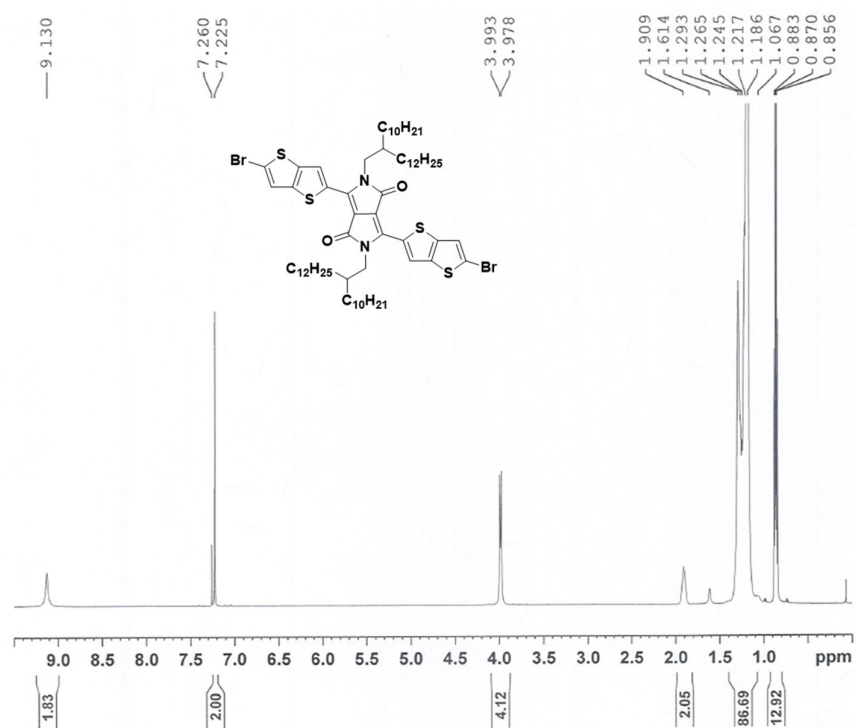
(a)  $^1\text{H}$  NMR spectrum (500MHz,  $\text{CDCl}_3$ ) of Br-T-DPP-T-Br



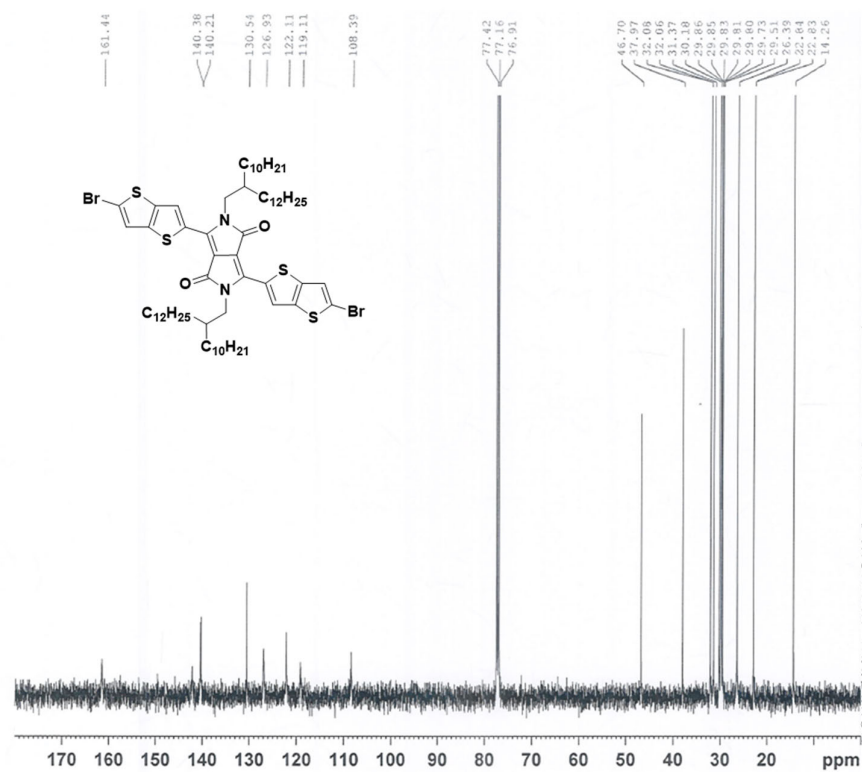
(b)  $^{13}\text{C}$  NMR spectrum (500MHz,  $\text{CDCl}_3$ ) of Br-T-DPP-T-Br



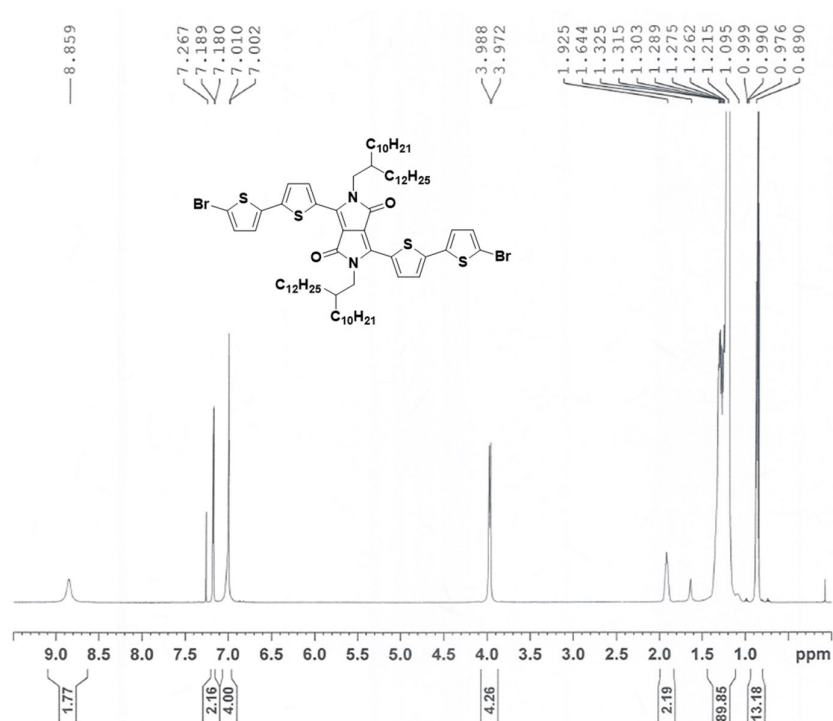
(c)  $^1\text{H}$  NMR spectrum (500MHz,  $\text{CDCl}_3$ ) of Br-TT-DPP-TT-Br



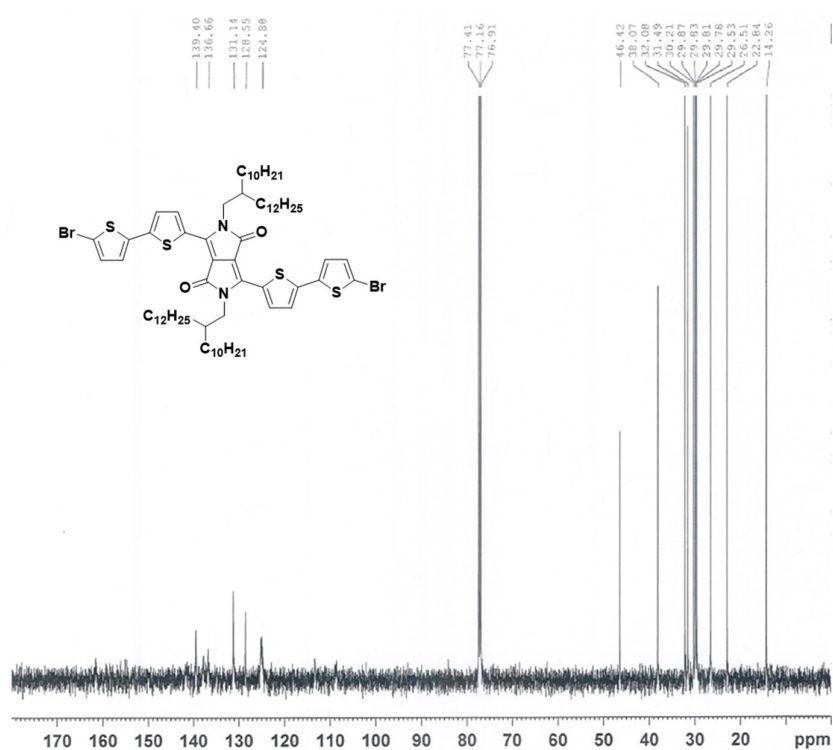
(d)  $^{13}\text{C}$  NMR spectrum (500MHz,  $\text{CDCl}_3$ ) of Br-TT-DPP-TT-Br



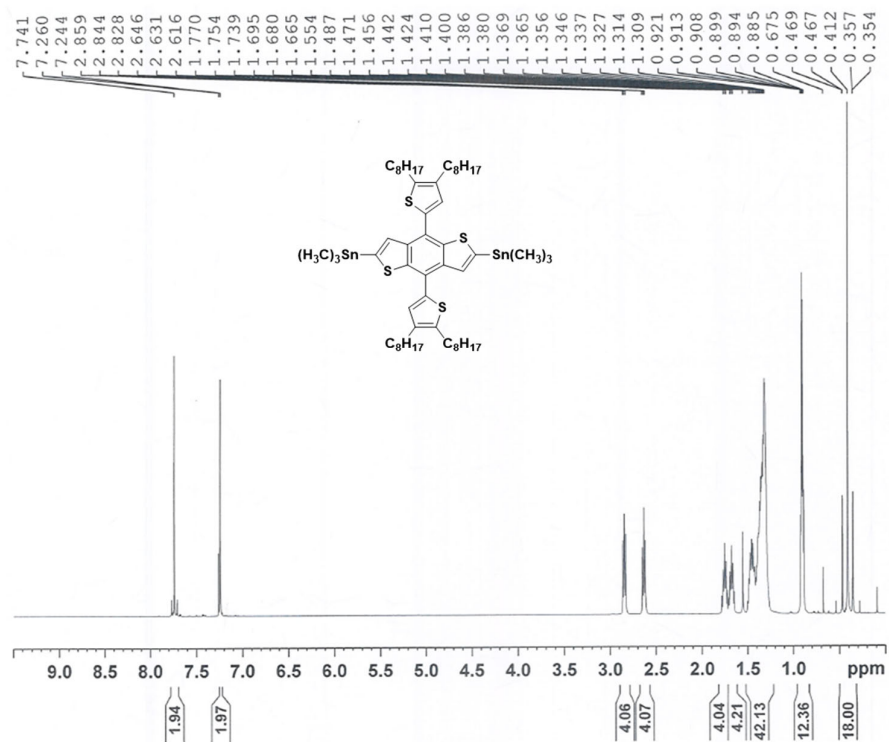
(e)  $^1\text{H}$  NMR spectrum (500MHz,  $\text{CDCl}_3$ ) of Br-BT-DPP-BT-Br



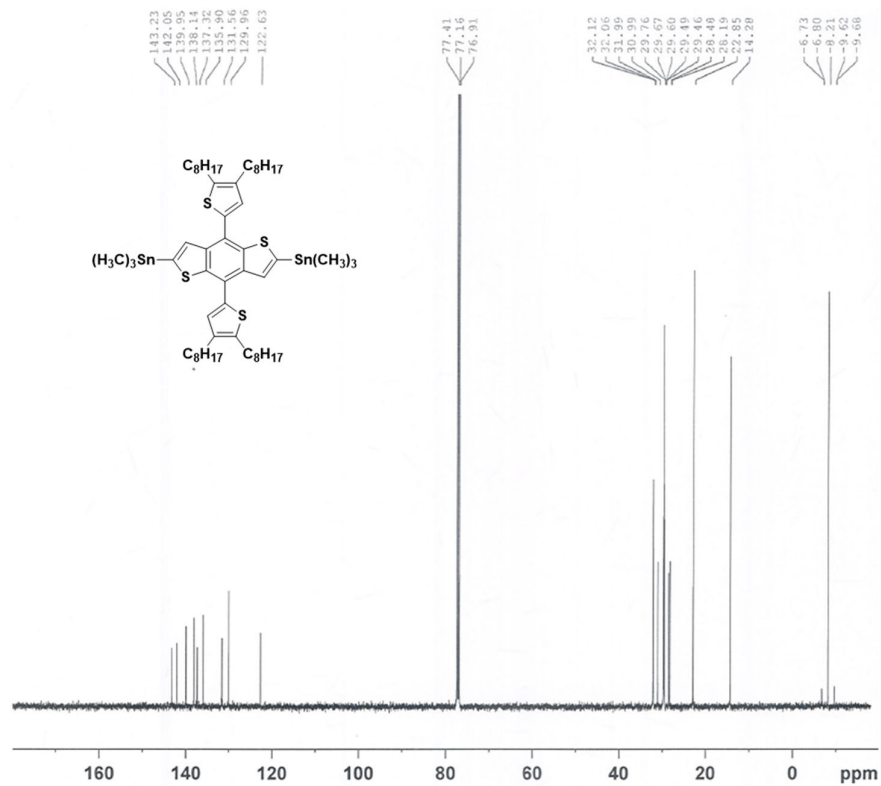
(f)  $^{13}\text{C}$  NMR spectrum (500MHz,  $\text{CDCl}_3$ ) of Br-BT-DPP-BT-Br



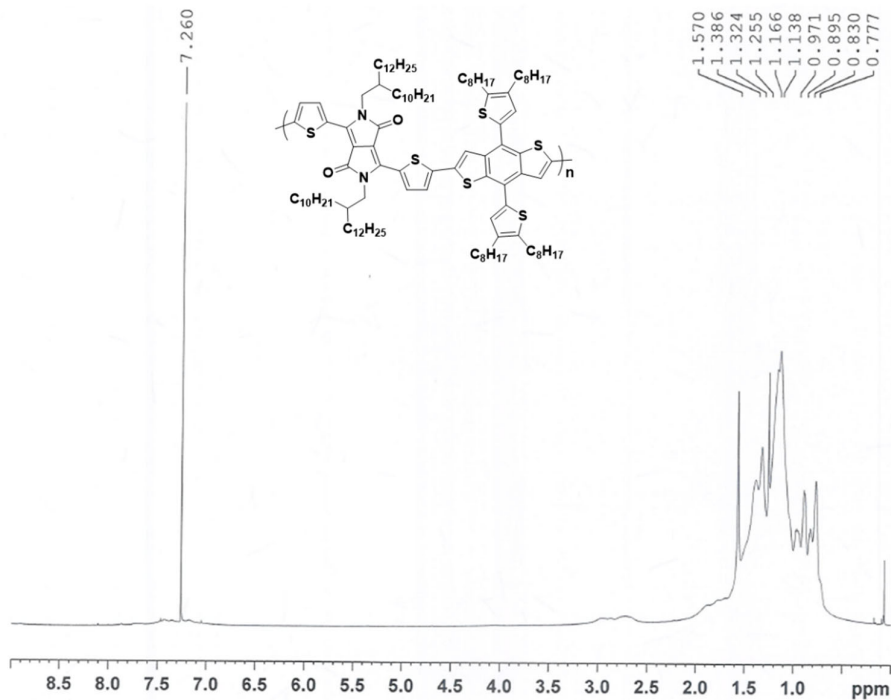
(g)  $^1\text{H}$  NMR spectrum (500MHz,  $\text{CDCl}_3$ ) of Tin-BDT-Tin



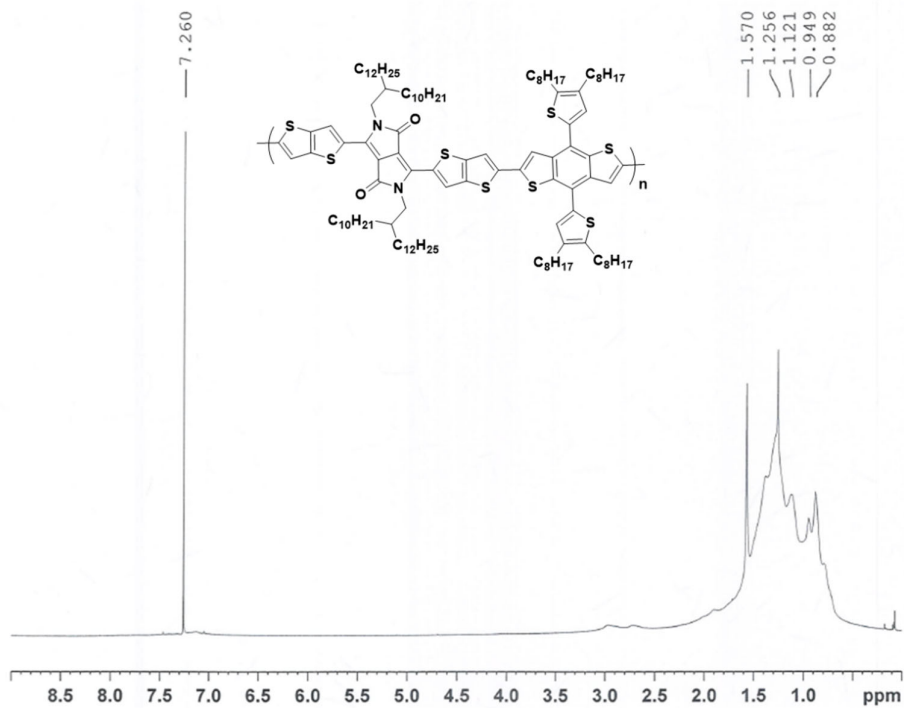
(h)  $^{13}\text{C}$  NMR spectrum (500MHz,  $\text{CDCl}_3$ ) of Tin-BDT-Tin



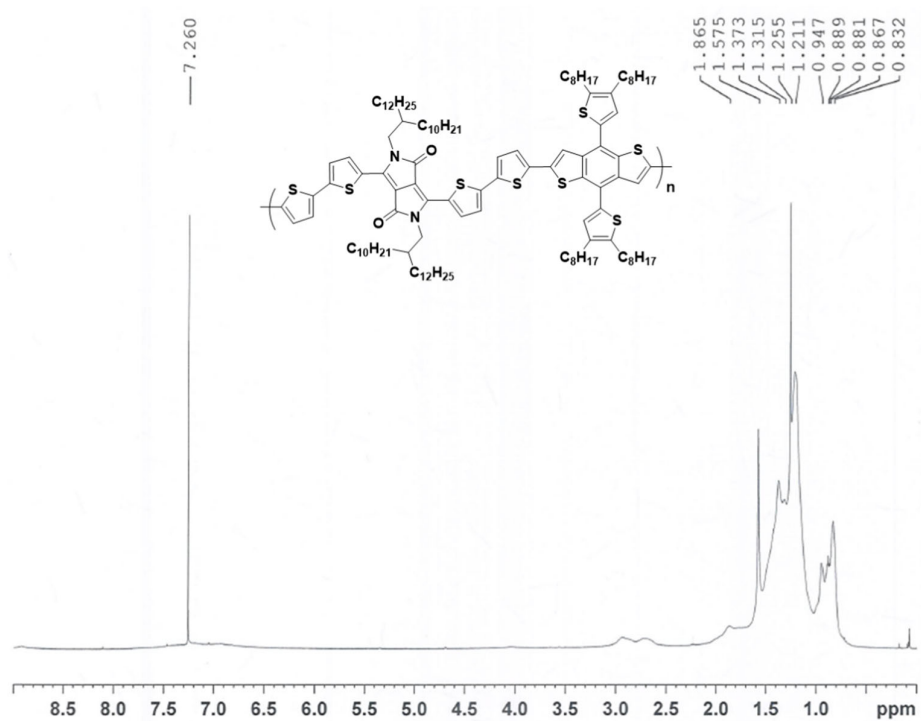
(i)  $^1\text{H}$  NMR spectrum (500MHz,  $\text{CDCl}_3$ ) of P1(T-DPP-T-BDT)



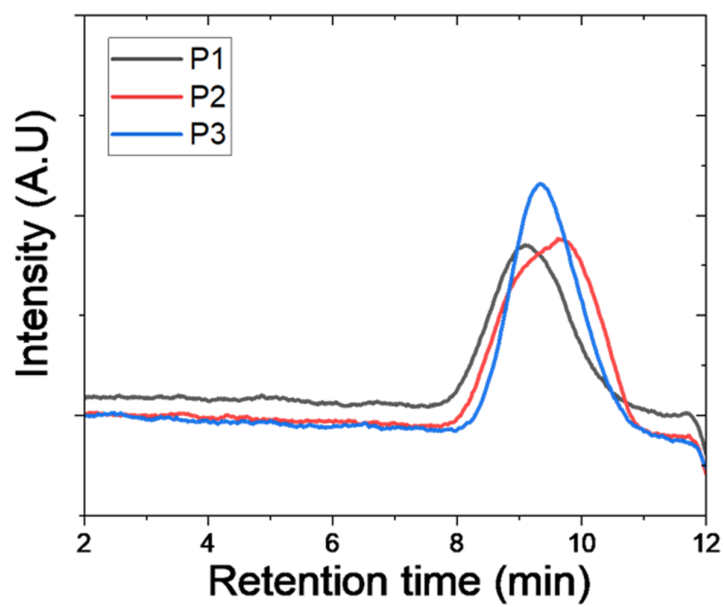
(j)  $^1\text{H}$  NMR spectrum (500MHz,  $\text{CDCl}_3$ ) of P2(TT-DPP-TT-BDT)



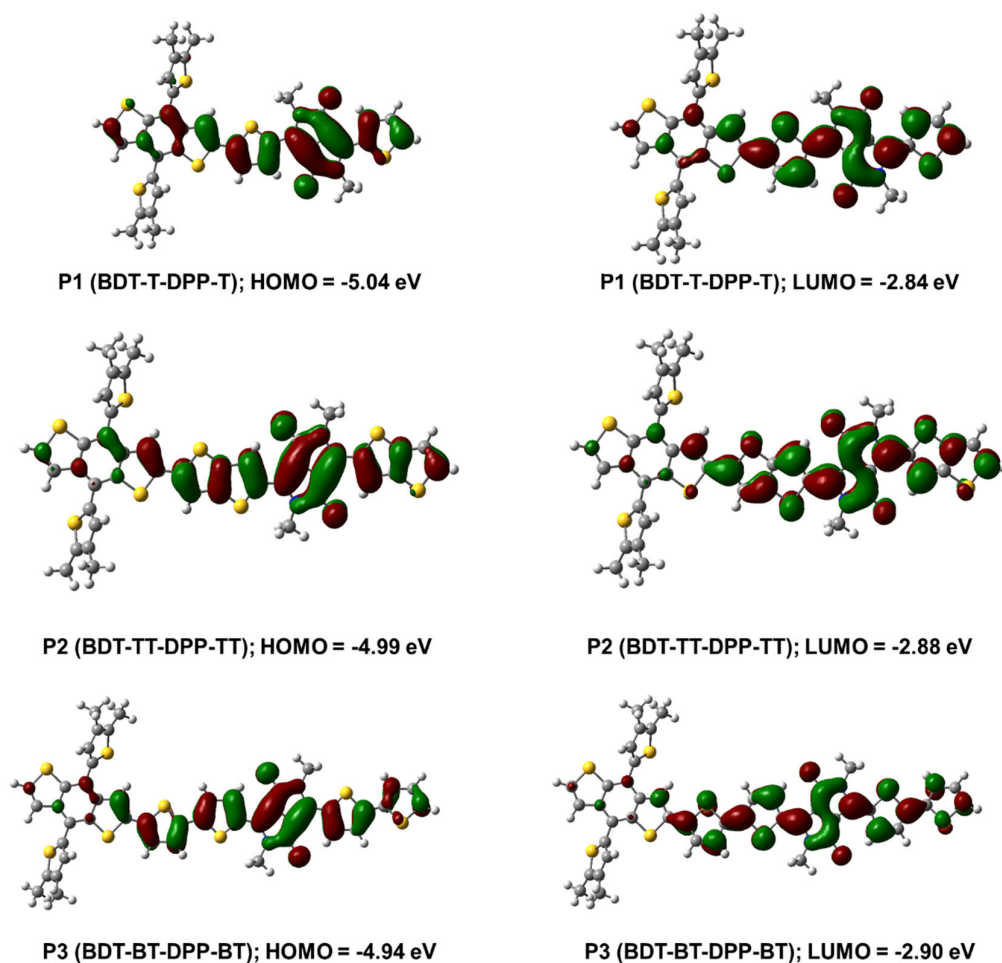
(k)  $^1\text{H}$  NMR spectrum (500MHz,  $\text{CDCl}_3$ ) of P3(BT-DPP-BT-BDT)



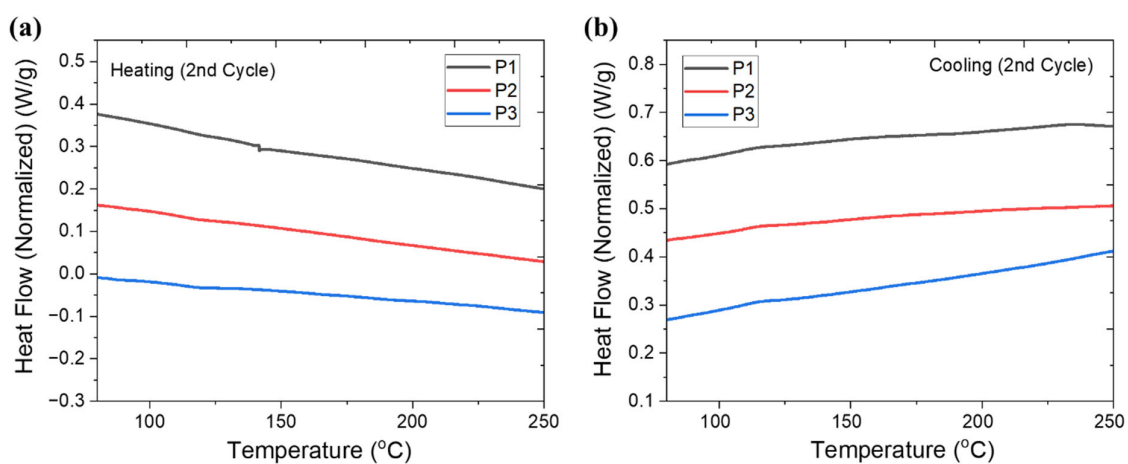
**Figure S2.** NMR characterizations of monomers (a-h) and polymers (i-k) used in this study



**Figure S3.** GPC profiles of three PDs (P1, P2, and P3)



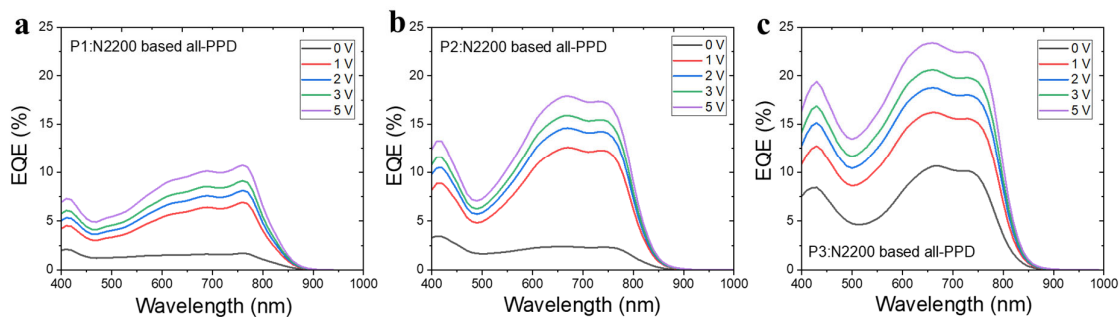
**Figure S4.** DFT calculation for estimation of HOMO/LUMO levels of P1, P2 and P3 polymers



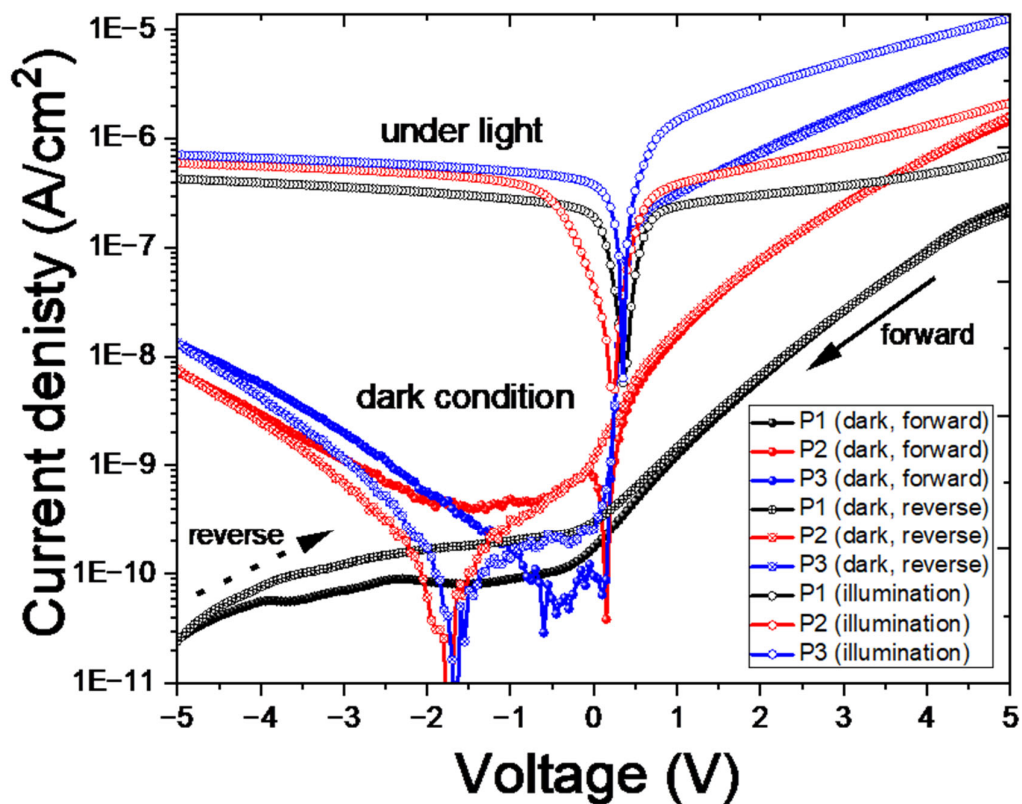
**Figure S5.** DSC measurements for P1, P2 and P3 ((a) 2nd cycle of heating, (b) 2nd cycle of



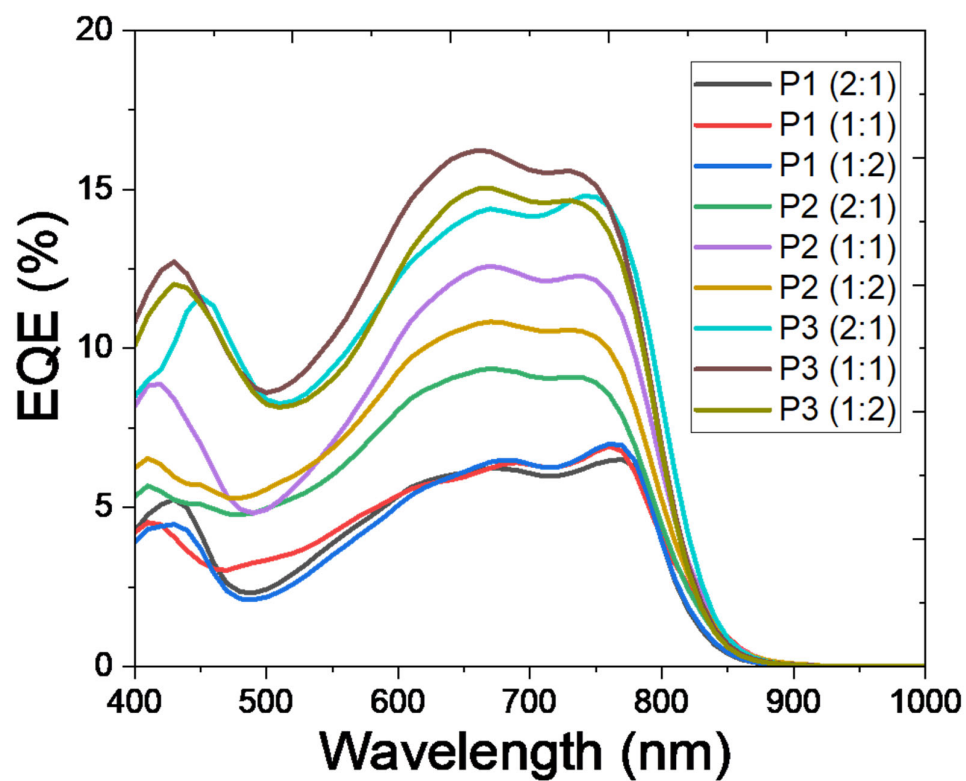
cooling)



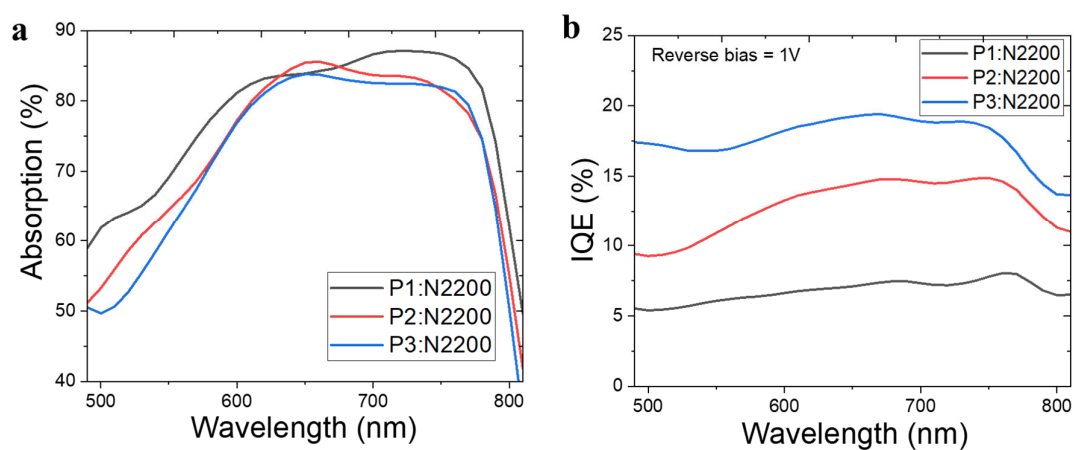
**Figure S6.** EQE vs bias dependency of P1 (a), P2 (b), and P3-based all-PPD devices (c)



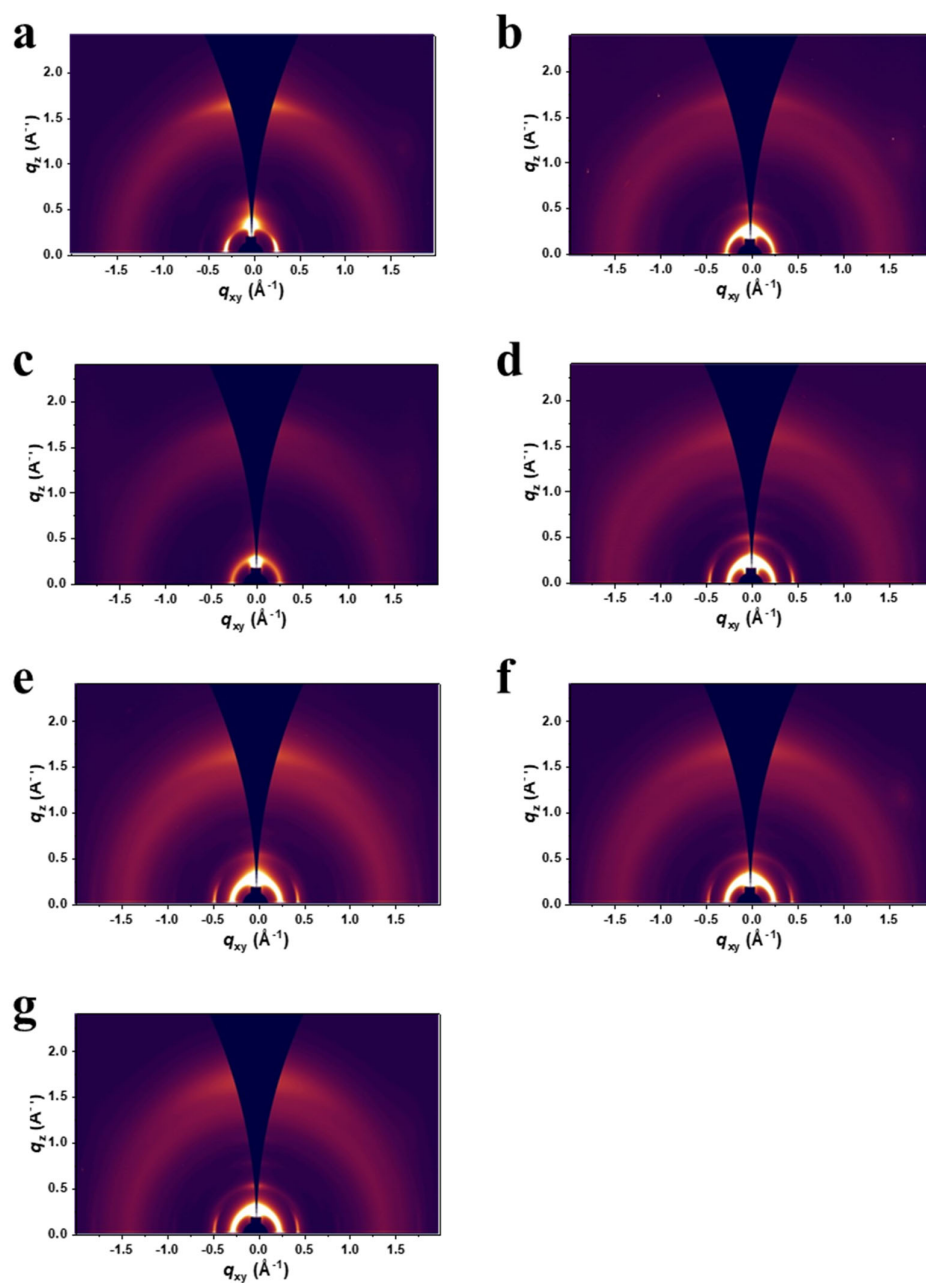
**Figure S7.** J-V curves of three Pds based all-PPDs under the dark condition (forward and reverse scan) and under the white light



**Figure S8.** EQE curves of three PDs based all-PPDs with different PD:PA weight ratios (reverse bias =  $-1\text{V}$ )



**Figure S9.** (a) Device absorption spectra, and (b) IQE spectra (reverse bias =  $1\text{V}$ ) of P1, P2, and P3 based all-PPDs.



**Figure S10.** GIXD reciprocal mapping images of pure polymers and all-polymer blends. (a) P1, (b) P2, (c) P3, (d) N2200; (e) P1:N2200, (f) P2:N2200, (g) P3:N2200.

**Table S1.** Material information of three PDs used in this study (Amount,  $M_n$ ,  $M_w$ , and PDI)

	Amount (mg)	$M_n$ (kg/mol)	$M_w$ (kg/mol)	PDI ( $M_w/M_n$ )
P1 (MC) (used in this study)	135.6	60.1	137.4	2.29

P1 (CF)	64.6	81.0	167.9	2.07
P2 (MC)	223.9	34.7	89.9	2.60
P2 (CF) (used in this study)	14.5	37.8	95.9	2.54
P3 (MC)	34.0	35.7	74.8	2.10
P3 (CF) (used in this study)	246.0	42.2	89.3	2.12

**Table S2.** Comparison of our work with representative OPDs based on all-polymer-based photo-active materials.

Ref.	Photo-active layers	Top electrode	Bottom electrode	Detectivity D* (Jones)	Wavelength (nm)
This work	P1:N2200	Ag	ITO	$8.3 \times 10^{12}$	720
	P3:N2200			$5.9 \times 10^{12}$	650
[16]	NT40 :PNDI-2T(N2200)	Al	ITO	$2.6 \times 10^{13}$	720
[33]	PTzBI-Ph :PNDI-2T(N2200)	Al	ITO	$5.7 \times 10^{12}$	600
[34]	PDPPT :PNDI	Al	ITO	$3.4 \times 10^{12}$	850
[35]	PDTP-DPP :PNDI	Al	ITO	$2.4 \times 10^{12}$	900
[36]	PBDP-T :PNDI-DTBT	Ag	ITO	$4.8 \times 10^{12}$	660
[37]	P3HT :PIDT-2TPD	Al	ITO	$1.1 \times 10^{12}$	610
[38]	PSBOTz :PNE	Ag	ITO	$1.8 \times 10^{12}$	532