

Supporting Information

Broadband polymer photodetectors with a good trade-off between broad response and high detectivity by using combined electron-deficient moieties

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Characterizations. ^1H and ^{13}C NMR spectra were acquired from a Bruker Avance 400 NMR spectrometer. The element analysis was performed on Vario EL Elemental Analysis Instrument. The molecular structures of the three polymers were confirmed with ^1H NMR spectroscopy and elemental analysis. The absorption spectra were conducted on a Shimadzu UV-3600 spectrophotometer. The molecular weight of the polymers was measured by gel permeation chromatography (GPC) method, with polystyrene as standards and chloroform (CHCl_3) as eluent at room temperature. Thermogravimetric analysis (TGA) was acquired on a PerkinElmer Pyris Diamond TG from 50 to 800 °C at a heating rate of 10 °C/min with a continuous nitrogen flow. Differential scanning calorimetry (DSC) was done on a TA-DSC Q100 from 20 °C to 350 °C with a heating/cooling rate of 10 °C/min under a nitrogen atmosphere.

Cyclic voltammetry (CV) was used to characterize electrochemical properties of the polymers. CV experiments were carried out on a CHI660b electrochemical workstation in acetonitrile solution containing $n\text{-Bu}_4\text{NPF}_6$ (0.1 M) at a scan speed of 50 mV/s. Pt disk (2 mm diameter), Pt plate, and Ag/AgCl were used as working electrode, counter electrode, and reference electrode, respectively. The polymer thin films for electrochemical measurements were obtained from a chloroform solution, ca. 5 mg/mL, onto a Pt disk electrode. Ferrocene was used as an internal standard of the redox potentials for calibration.

The out-of-plane grazing incidence X-ray diffraction (GIXD) were measured on a Bruker D8 Discover reflector, with a step-scan rate of 0.05° per 5 s and the scattering

angle 2-theta ranging from 2° to 30°. The solid samples were obtained by spin-coating from concentrated polymer solutions (10 mg/mL) in chloroform on glass substrates.

Atomic force microscopy (AFM) was performed on a SPA300HV instrument equipped with a SPI3800N controller (Seikoin Instruments, Japan) in tapping mode under ambient conditions using silicon cantilevers (Applied Nanostructures, nominal spring constant of 2.0 N/m and nominal resonance frequency of ~75 kHz).

Photodetector Fabrication and Characterizaion. The PPDs devices with the structure of ITO/PEDOT:PSS/Polymer:PC₇₁BM/ZnO/Al were fabricated with the following steps: ITO-coated glass substrates were cleaned sequentially in ultrasonic baths with acetone, deionized water, and isopropyl alcohol, and then dried at 120 °C for 1h. A thin layer of PEDOT:PSS (Baytron P VP Al 4083, 30 nm) was deposited on UV-ozone treated ITO at 3000 rpm for 60 s, and then baking for 30 min at 120 °C in the air. Each active blending solution (total of 24 mg mL⁻¹, polymer: PC₇₁BM, 1:2 w/w) for spin-coating contained 3% of 1, 8-diiodooctane (DIO) by volume as the additive in chlorobenzene. The blending solution was spin-coated at 1500 rpm for 40 s under nitrogen atmosphere, making the thickness of P1:PC₇₁BM, P2:PC₇₁BM and P3:PC₇₁BM as 100, 95, and 104 nm, respectively. A butanol solution of ZnO was deposited on the active layer at 1500 rpm for 40s, giving a ZnO layer of 20 nm. The Al (100 nm) layer was subsequently deposited on the surface of ZnO under high vacuum (3×10⁻⁴ Pa). Two pixels, each with an active area of 0.16 cm², were fabricated per ITO. EQE measurements were measured under ambient conditions using the equipment from

Beijing 7-Star Optical Instruments Co., Ltd. Incident light from a 250 W halogen lamp passing through two cascade monochromators was chopped at 25 Hz and concentrated on the active area of the device. The photocurrent signal was amplified by a low-noise current amplifier (DLPCA-200, Femto) and then detected with a lock-in amplifier (SR830, Stanford Research Systems). Keithley 236 Source Measure unit was used to measure the dark current density–voltage (J – V curve) properties of the devices.

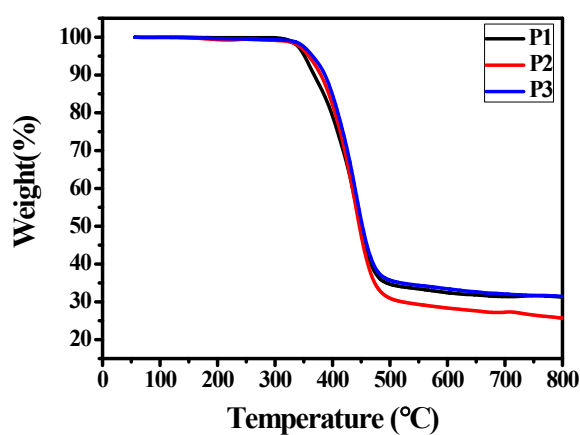


Figure S1. TGA thermograms of polymers under nitrogen flow.

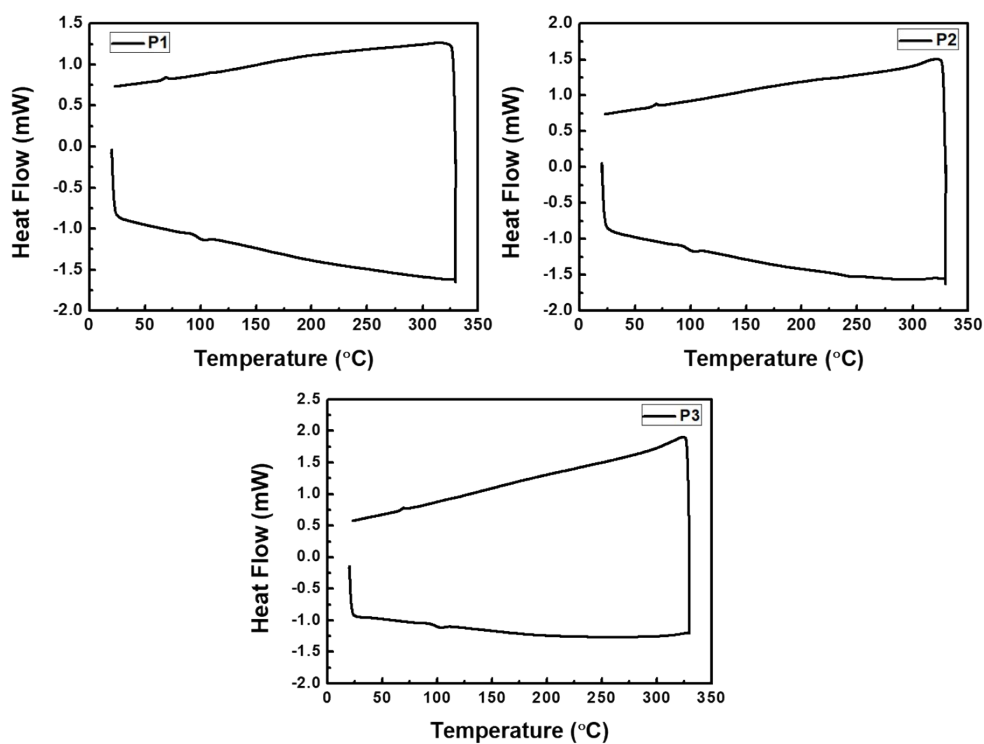


Figure S2. The second heating and cooling DSC scans of polymers under nitrogen flow.

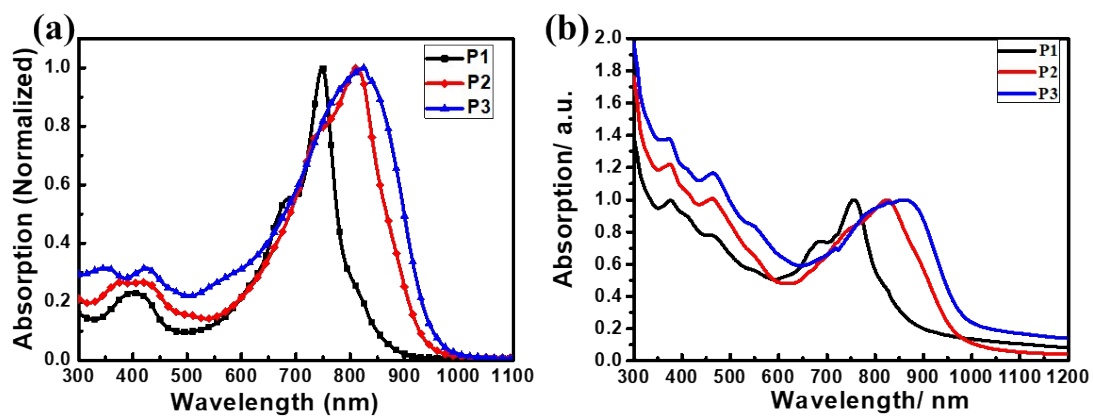
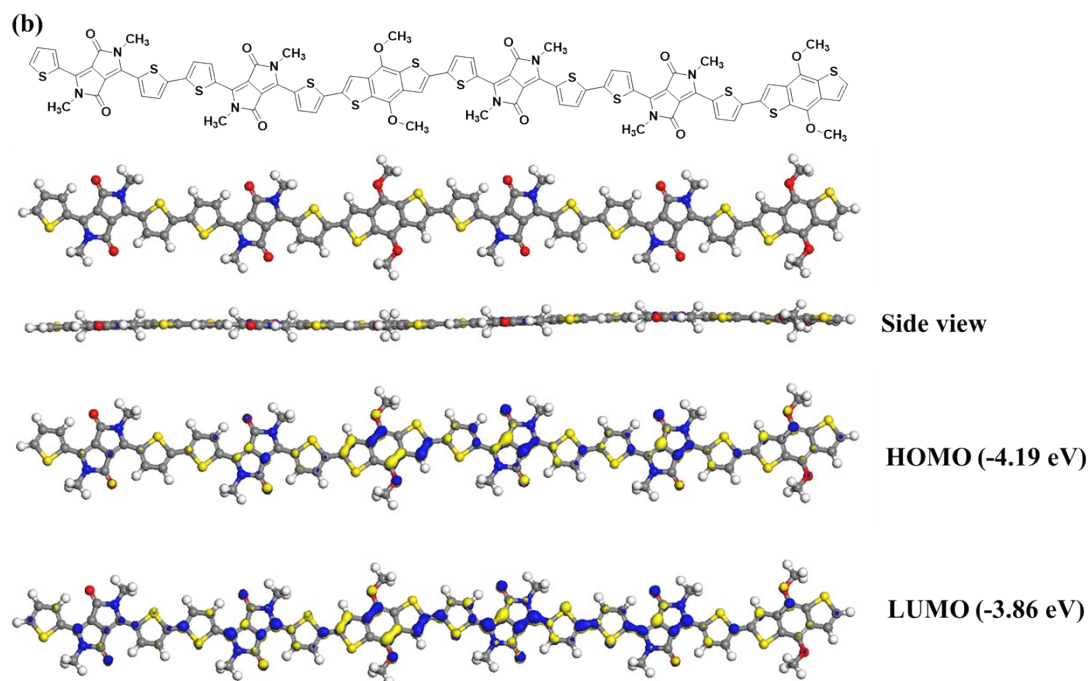
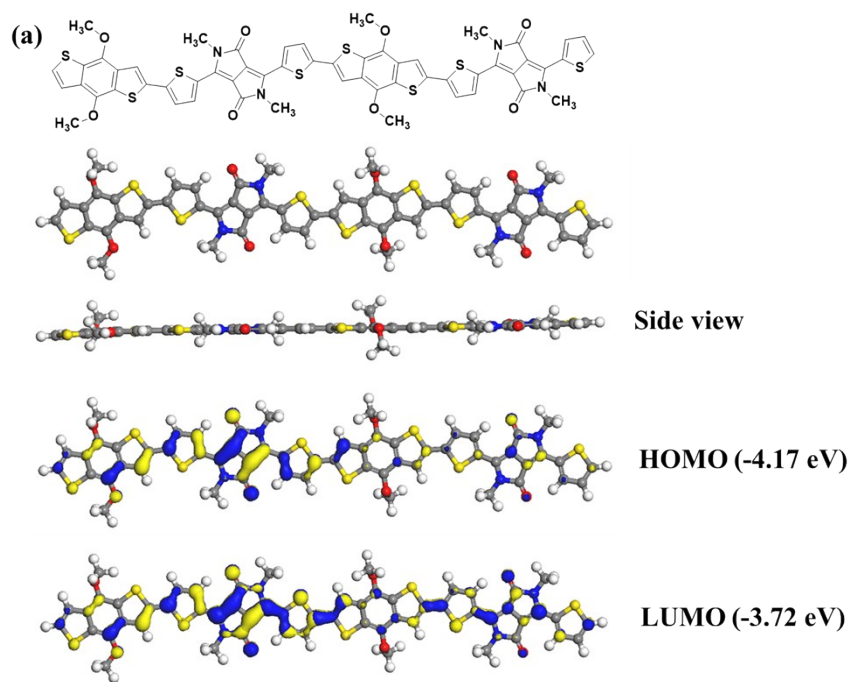


Figure S3. (a) The absorption of the polymers in dilute chlorobenzene solution (0.03 g/L); (b) The absorption of the blend films of polymers:PC₇₁BM.



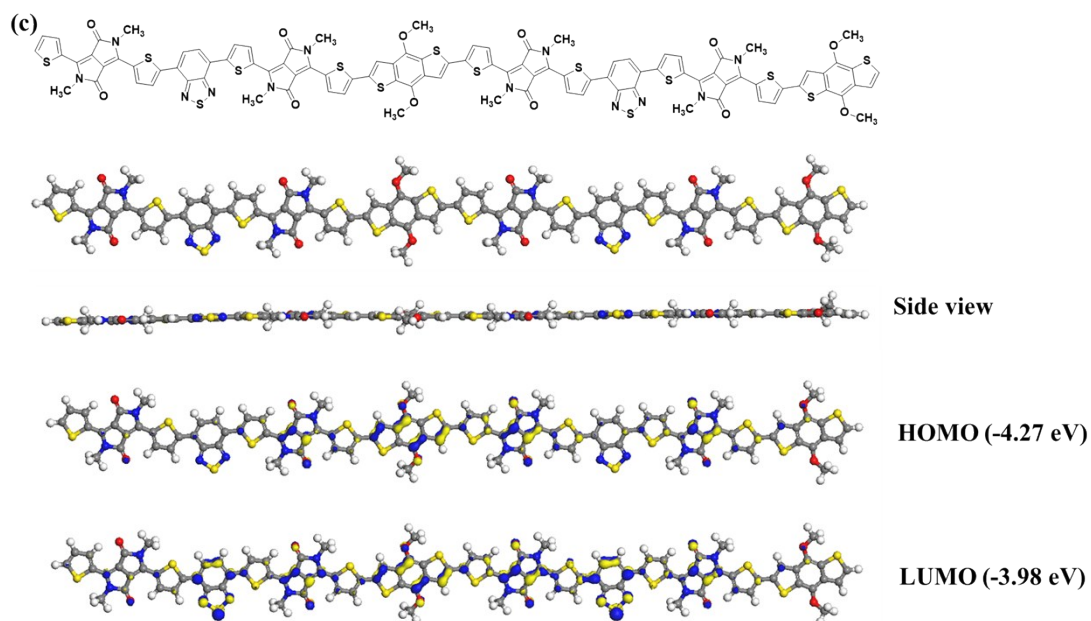


Figure S4. The optimized geometry and frontier molecular orbitals of P1 (a), P2 (b) and P3 (c) dimers based on DFT calculations

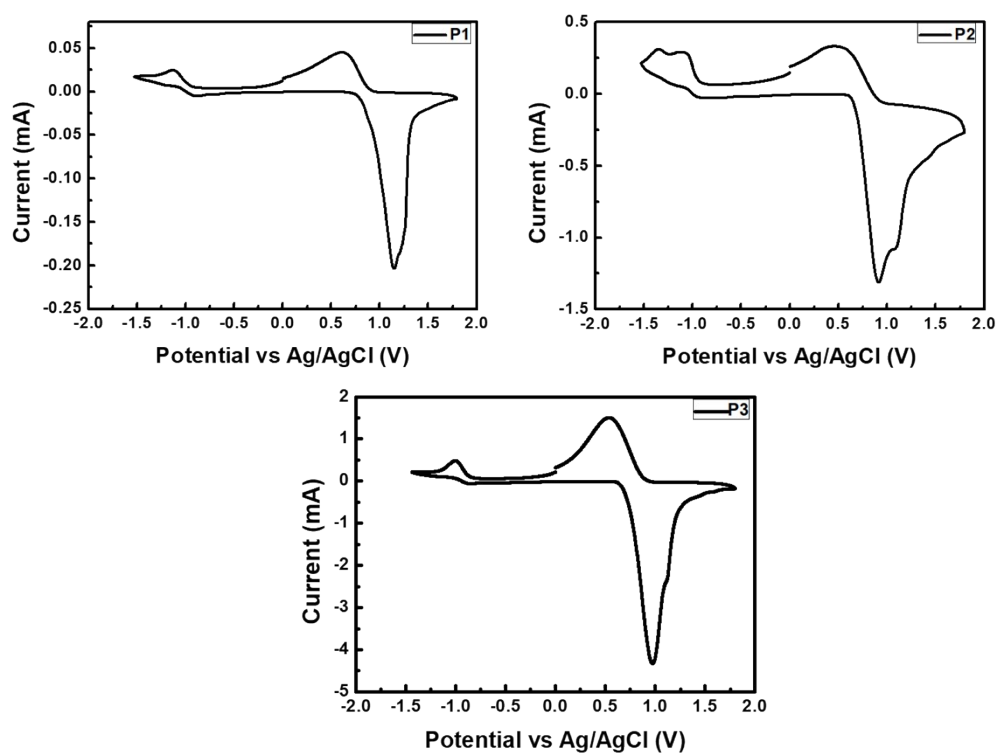


Figure S5. Cyclic voltammograms of polymer films on Pt electrode in 0.1 M *n*-Bu₄NPF₆ solution in dry acetonitrile with a scan rate of 50 mV/s.

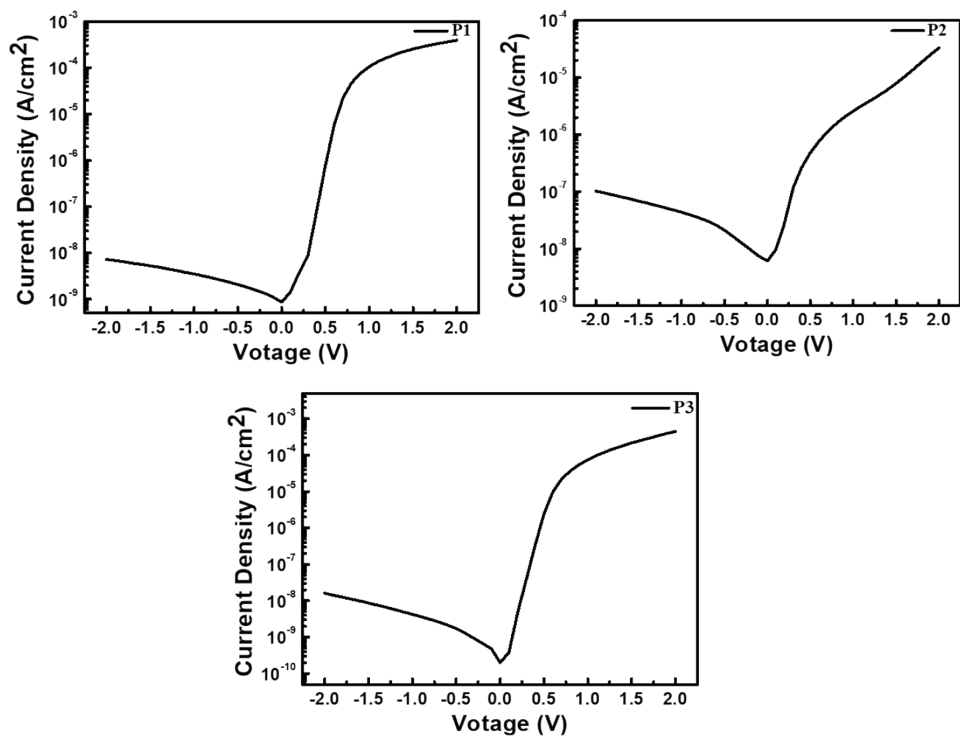


Figure S6. The dark current density of the polymer photodetectors.

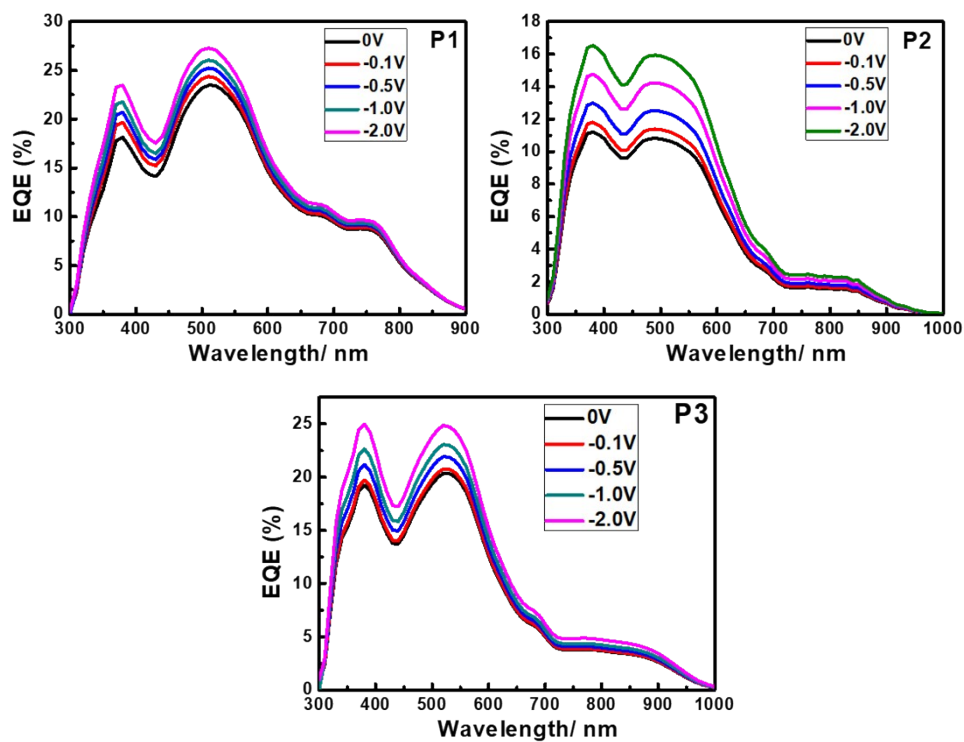


Figure S7. The spectral EQE of the polymer photodetectors.

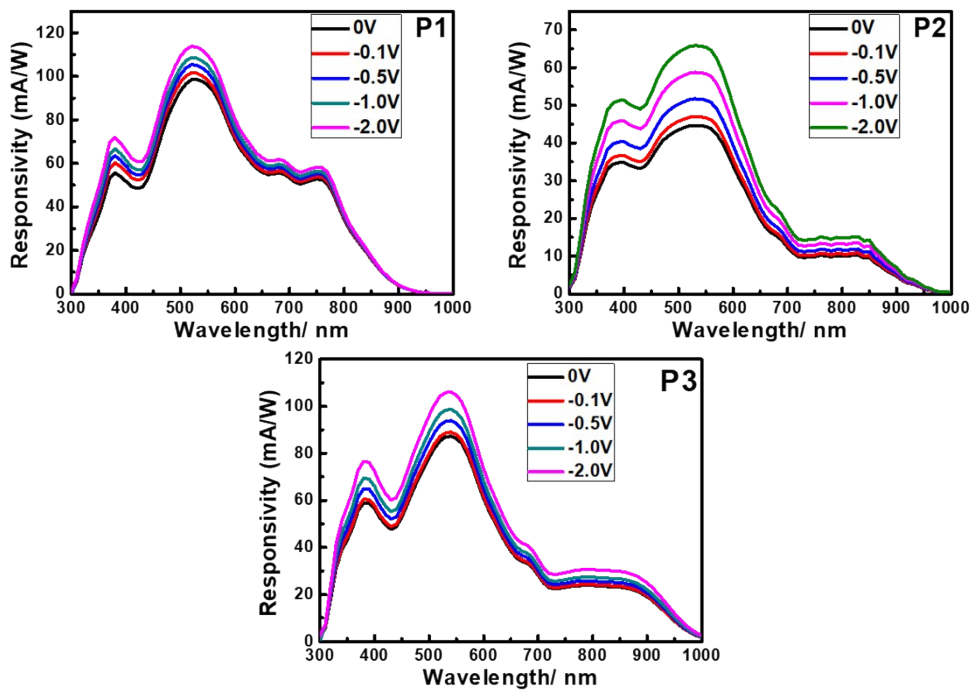


Figure S8. The spectral responsivity of the polymer photodetectors.

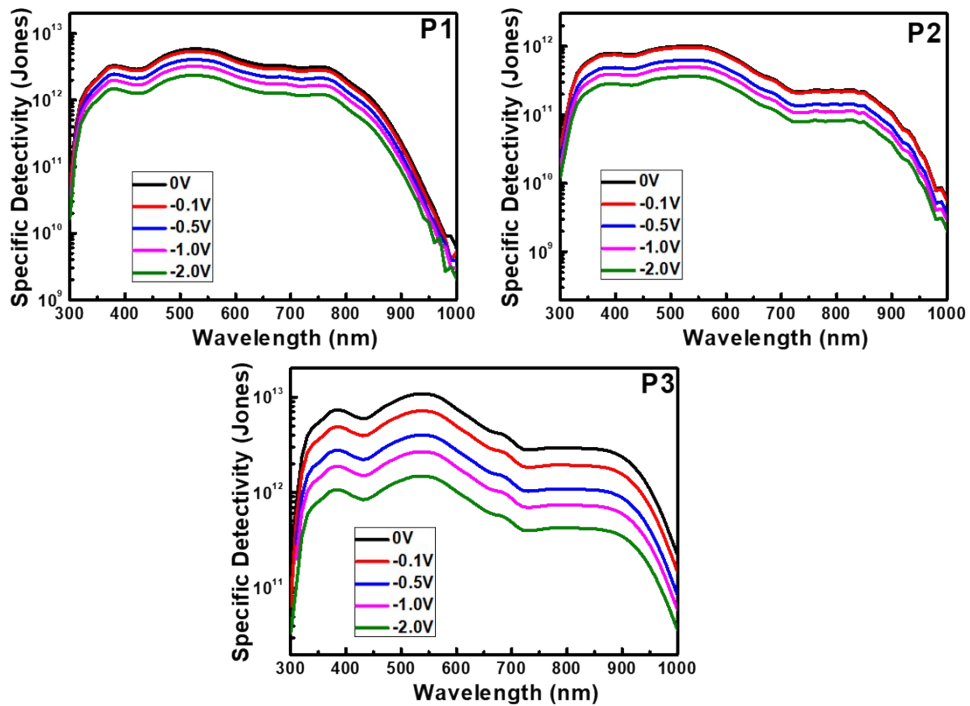


Figure S9. The spectral specific detectivity of the polymer photodetectors.

Table S1. Polymer photodetector optimization for the devices based on P1, P2 and P3.

Blend film	Ratio D:A	Total conc. mg/ml	Additive ^a v/v %	J_d^b (A/cm ²)	$D^*_{900nm}^b$ (Jones)	Layer Thickness ^c (nm)
P1:PC ₇₁ BM	1:3	32	DIO 1	9.2×10^{-9}	1.3×10^{10}	90-140
	1:2	24	DIO 1	4.1×10^{-9}	8.9×10^{10}	80-130
	1:2	24	DIO 3	1.1×10^{-9}	2.0×10^{11}	80-130
	1:2	24	DIO 5	3.1×10^{-9}	6.3×10^{10}	80-130
P2:PC ₇₁ BM	1:3	32	DIO 1	3.5×10^{-8}	4.3×10^{10}	90-140
	1:2	24	DIO 1	1.3×10^{-8}	6.8×10^{10}	80-130
	1:2	24	DIO 3	7.4×10^{-9}	1.0×10^{11}	80-130
	1:2	24	DIO 5	9.1×10^{-9}	8.5×10^{10}	80-130
P3:PC ₇₁ BM	1:3	32	DIO 1	5.1×10^{-9}	4.8×10^{11}	100-140
	1:2	24	DIO 1	1.6×10^{-9}	8.5×10^{11}	80-130
	1:2	24	DIO 3	4.8×10^{-10}	1.6×10^{12}	80-130
	1:2	24	DIO 5	8.3×10^{-10}	1.0×10^{12}	80-130

- a) 1,8- diiodooctane (DIO).
b) Dark current density and specific detectivity at -0.1 V.
c) Thickness variation is realized by the different spin speeds.

Table S2. Device performance of some reported polymer photodetectors.

Active layer	J_d (A/cm ²)	D^*_{500nm} (Jones)	D^*_{900nm} (Jones)	References
PDPP3T:PC₇₁BM	6.4×10^{-10} (-0.5V)	1.1×10^{13} (-0.5V)	5.0×10^{12} (-0.5V)	<i>Adv. Optical Mater.</i> 2015 , 3, 1570–1576
PBBTPD:Tri-PC₆₁BM	1.0×10^{-6} (-0.5V)	1.7×10^{11} (-0.5V)	1.8×10^{11} (-0.5V)	<i>J. Mater. Chem. C</i> , 2018 , 6, 3634-3641
PDDTT:PC₆₁BM	1.1×10^{-9} (-0.1V)	2.2×10^{12} (-0.1V)	1.2×10^{12} (-0.1V)	<i>Adv. Funct. Mater.</i> 2014 , 24, 7605-7612
PBT(EDOT):PC₆₁BM	1.6×10^{-10} (-0.2V)	2.1×10^{13} (-0.2V)	no response	<i>Adv. Mater.</i> , 2015 , 27, 6496-6503
PTB7-Th:cP₄	1.5×10^{-10} (-0.1V)	1.3×10^{13} (-0.1V)	no response	<i>J. Am. Chem. Soc.</i> , 2016 , 138, 16426–16431
NT40:N2200	4.8×10^{-10} (-0.1V)	1.6×10^{13} (-0.1V)	no response	<i>ACS Appl. Mater. Interfaces</i> 2019 , 11, 14208-14214
P3HT:P1	1.5×10^{-6} (-1.0V)	1.4×10^9 (-1.0V)	2.0×10^8 (-1.0V)	<i>Chem. Mater.</i> 2019 , 31, 7657-7665
PTTBAI:PC₇₁BM	2.1×10^{-7} (-2.0V)	6.0×10^{11} (-2.0V)	7.0×10^{11} (-2.0V)	<i>J. Mater. Chem. C</i> , 2018 , 6, 11645--11650
PDPP-FBT:PC₇₁BM	1.2×10^{-8} (-0.5V)	1.7×10^{12} (-0.5V)	4.0×10^{11} (-0.5V)	<i>Org. Electron.</i> 2019 , 64, 274-279
P3:PC₇₁BM	4.8×10^{-10} (-0.1V)	7.1×10^{12} (-0.1V)	1.6×10^{12} (-0.1V)	This work
	1.7×10^{-9} (-0.5V)	3.6×10^{12} (-0.5V)	8.8×10^{11} (-0.5V)	
	4.2×10^{-9} (-1.0V)	2.4×10^{12} (-1.0V)	6.0×10^{11} (-1.0V)	
	1.6×10^{-8} (-2.0V)	1.3×10^{12} (-2.0V)	3.5×10^{11} (-2.0V)	

^1H NMR spectrum of Polymers.

