Supporting Information

Low-LUMO acceptor polymers for high-gain all-polymer photodiodes

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1. Materials and methods

All the chemicals and reagents were obtained from commercial sources and used without further purification. The solvents were purified by distillation. All the reactions and operations were carried out under argon by employing the standard Schlenk techniques. The NMR spectra were recorded on a Bruker AV400 NMR Spectrometer. Gel permeation chromatography was performed on a Waters 2414 system with 1,2,4-trichlorobenzene as eluent and polystyrene as standards at 150 ^{o}C. Cyclic voltammetry was done on a CHI660b electrochemical workstation in a solution of n-Bu_4NPF_6 in dry acetonitrile (0.1M) with the scan rate of 50 mV/s at room temperature under Ar atmosphere. The absorption spectra of polymers were recorded on a Shimadzu UV3600 spectrophotometer. The out-of-plane GIXRD profiles were obtained using a Bruker D8 Discover reflector. The in-plane GIXRD profiles were performed using a Rigaku SmartLab X-ray di□ractometer. The AFM images were obtained using a SPI3800N AFM (Seiko Instruments Inc., Japan).

For a typical polymer photodetector, we can consider the shot noise from the dark current as the major contributor to the total noise. Thus, specific detectivity can be expressed as:

$$D^{*}=R/(2qJ_d)^{1/2}=(J_{ph}/L_{light})/(2qJ_d)^{1/2} \text{ (Jones)}$$

where J_d is the dark current density (A/cm^2) and q is the absolute value of electron charge (1.6 x 10^{-19} Coulombs). R is the spectral responsivity, a ratio of photocurrent (J_{ph}) to incident- light intensity (L_{light}).[1] R also can be expressed as:

$$R = (EQE\lambda)/1240 \text{ (A/W)}$$

where λ is the wavelength of the corresponding EQE. In this work, specific detectivity can be calculated by the equation:

$$D^*=R/(2qJ_d)^{1/2}= (EQE\lambda)/[1240(2qJ_d)^{1/2}] \text{ (Jones)}$$

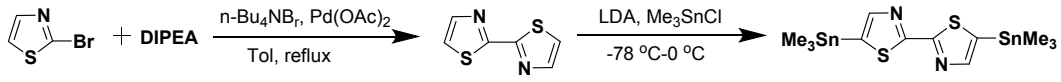
The detectivity calculated from the equation would be probably larger than the real value because the actual device noise might be higher due to the existence of other fundamental noise, such as 1/f noise.[2]

2. Synthesis

BTz-2Sn was synthesized according to the literature.[3], TT-2Sn and TTf-2Sn were purchased from SunaTech Inc. (Suzhou, China), NDI-2Br was obtained from Derthon Optoelectronic Materials Science Technology Co LTD (Shenzhen, China).

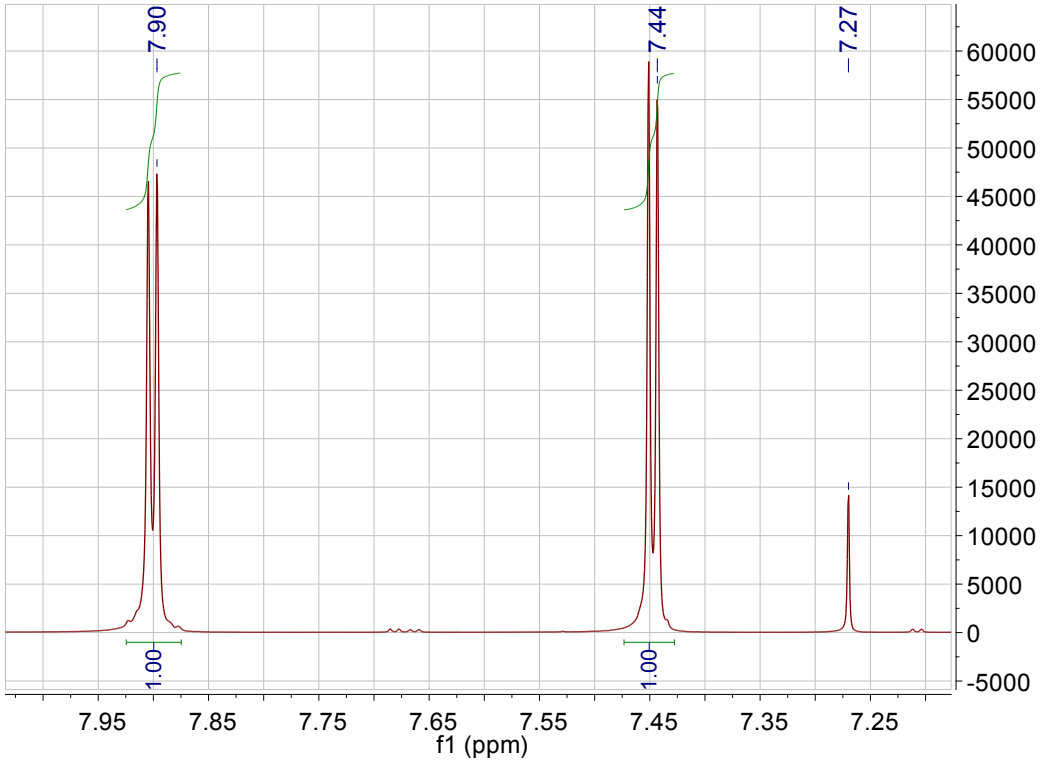
2.1 The synthesis of BTz-2Sn

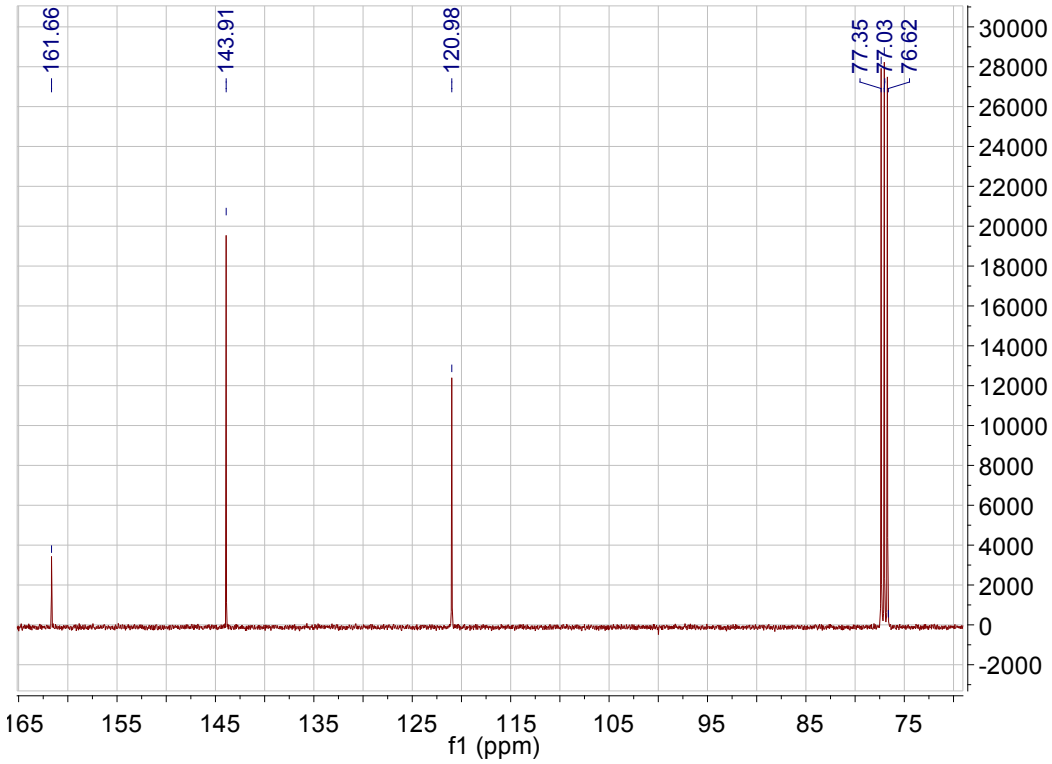
Scheme S1



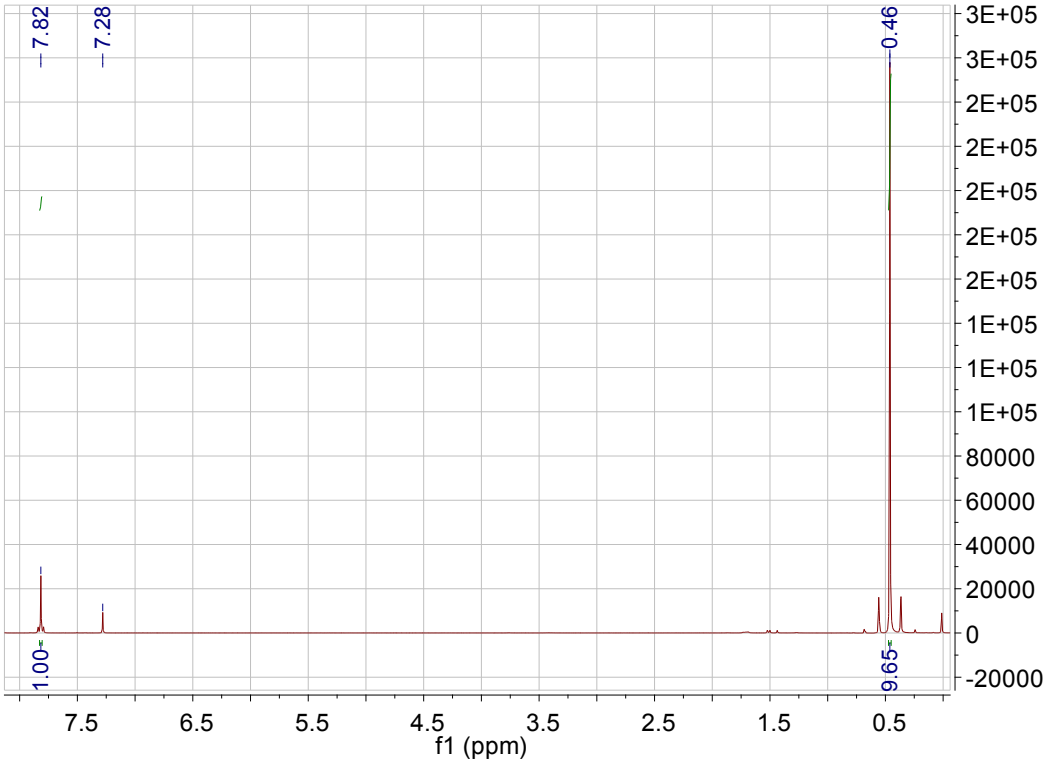
2-Bromothiazole **2,2'-Bithiazole** **BTz-2Sn**

2,2'-Bithiazole: 2-Bromothiazole (8.201 g, 50 mmol), N,N-diisopropylethylamine (DIPEA) (6.5 g, 50 mmol), n-Bu_4NBr (8.1 g, 25 mmol) and anhydrous toluene (120 mL) were added to a dried 250-mL Schlenk tube. The mixture was purged by argon for 15 min, then $Pd(OAc)_2$ (0.6 g, 2.5 mmol) was added. The reaction medium was then stirred for 24 h at 130 °C under argon. When the reaction finished, the solution was poured into 200 mL deionized water and the mixture was extracted into dichloromethane (200 mL). The organic solution was washed with brine (6 x 100 mL), then dried over anhydrous $MgSO_4$ for 3 h. Finally, the organic solution was concentrated with rotary evaporator. The resultant residue was purified by column chromatography (silica gel, hexane/DCM, 1:8 v/v), followed by recrystallization from cyclohexane to afford 2,2'-bithiazole as needle-like colorless crystals. (yield: 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm: 7.90 (dd, 2H), 7.44 (dd, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ/ppm:161.66, 143.91, 120.98.


7.90
7.44
7.27
1.00
1.00
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
7.95
7.85
7.75
7.65
7.55
7.45
7.35
7.25
f1 (ppm)

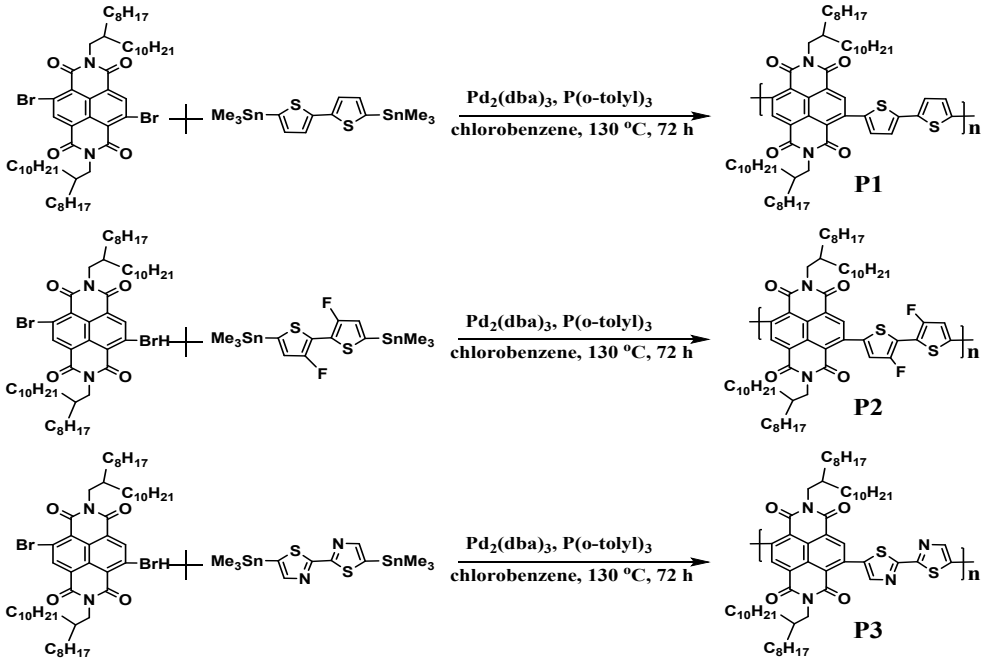

161.66
143.91
120.98
77.35
77.03
76.62
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
165
155
145
135
125
115
105
95
85
75
f1 (ppm)

BTz-2Sn: Diisopropylamine (1.2 mL) was added into THF (30 mL) under argon, then the mixed solution was cooled to -78 °C, followed by the dropwise of n-BuLi (2.7 mL, 2.5 M in THF). The resulting solution was warmed naturally to room temperature and stirred for 0.5 h to afford lithium diisopropylamide (LDA). Then the mixed solution was transferred and dropwise added to stirred solution of 2,2'-bithiazole (408 mg, 2.4 mmol) in 50 mL THF at -78 °C. After stirring at -78°C for 1 h, the resulting solution was warmed naturally to room temperature and stirred for another 0.5 h, then the solution was cooled to -78 °C and $SnMe_3Cl$ (9 mL) was added in a dropwise manner. The resulting solution was then warmed naturally to room temperature and stirred for 15 h. When the reaction finished, the solution was poured into 100 mL deionized water and extracted with DCM, then the organic solution was washed with brine (5 x 80 mL) and dried over anhydrous $MgSO_4$ for 3 h. Finally, the organic solution was concentrated with rotary evaporator. The resultant residue was purified by recrystallization from n-hexane to afford colorless needle like crystals. (yield: 75%). ^1H NMR ($CDCl_3$, 400 MHz): δ/ppm: 7.82 (s, 2H), 0.46 (s, 18H).



2.2 The synthesis of polymers

Scheme S2



P1: Compound **TT-2Sn** (98.4 mg, 0.20 mmol), compound **NDI-2Br** (197 mg, 0.20 mmol) and anhydrous chlorobenzene (5 mL) were added to a dried Schlenk tube. The mixture was purged by argon for 15 min, then $Pd_2(dba)_3$ (5 mg) and P(o-Tolyl)$_3$ (6 mg) were added. The reaction medium was then stirred for 72 h at 130 °C under argon. Then 0.2 mL of 2-bromothiophene was added to it after which stirred for further 12 h. After cooling to room temperature, the polymer was precipitated into methanol (300 mL) and filtered, then dried in vacuum drying oven. The polymer was washed in Soxhlet extractor with acetone and hexane overnight. The final product was dried under reduced pressure at room temperature to obtain a black solid (90% yield). GPC: Mn = 29.2 kDa, Mw = 61.32 kDa, PDI = 2.1.

P2: Compound **TTf-2Sn** (105.6 mg, 0.20 mmol), compound **NDI-2Br** (197 mg, 0.20 mmol) and anhydrous chlorobenzene (5 mL) were added to a dried Schlenk tube. The mixture was purged by argon for 15 min, then $Pd_2(dba)_3$ (5 mg) and P(o-Tolyl)$_3$ (6 mg) were added. The reaction medium was then stirred for 72 h at 130 °C under argon. Then 0.2 mL of 2-bromothiophene was added to it after which stirred for further 12 h. After cooling to room temperature, the polymer was precipitated into methanol (300 mL) and filtered, then dried in vacuum drying oven. The polymer was washed in Soxhlet extractor with acetone and hexane overnight. The final product was dried

under reduced pressure at room temperature to obtain a black solid (95% yield). GPC: Mn = 21.0 kDa, Mw = 48.3 kDa, PDI = 2.3.

P3: Compound **BTz-2Sn** (99.0 mg, 0.20 mmol), compound **NDI-2Br** (197 mg, 0.20 mmol) and anhydrous chlorobenzene (5 mL) were added to a dried Schlenk tube. The mixture was purged by argon for 15 min, then $Pd_2(dba)_3$ (5 mg) and P(o-Tolyl)$_3$ (6 mg) were added. The reaction medium was then stirred for 72 h at 130 °C under argon. Then 0.2 mL of 2-bromothiophene was added to it after which stirred for further 12 h. After cooling to room temperature, the polymer was precipitated into methanol (300 mL) and filtered, then dried in vacuum drying oven. The polymer was washed in Soxhlet extractor with acetone and hexane overnight. The final product was dried under reduced pressure at room temperature to obtain a black solid (85% yield). GPC: Mn = 20.3 kDa, Mw = 105.56 kDa, PDI = 5.2.

3. Characterizations of polymers

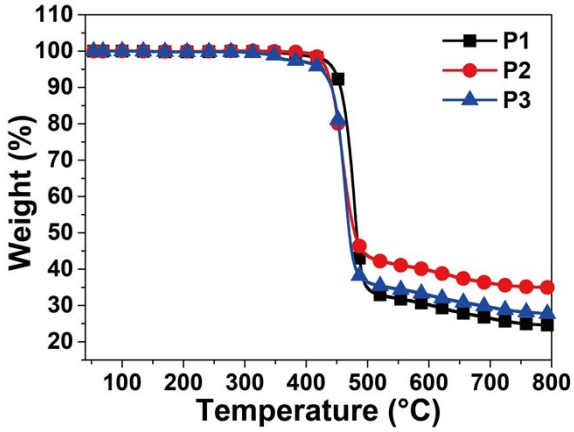


Figure S1. TGA thermograms of polymers under nitrogen flow.

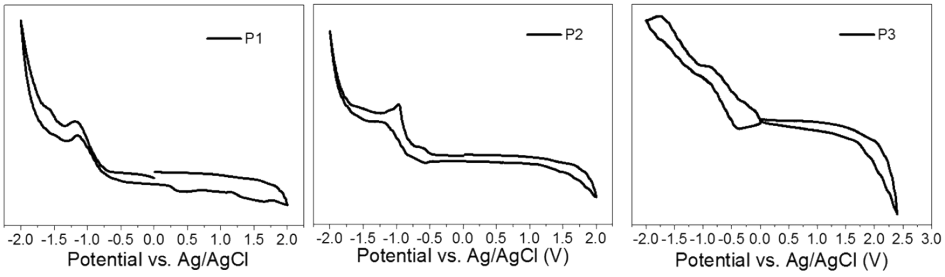


Figure S2. Cyclic voltammograms of polymer films on Pt electrode in 0.1 M n-Bu_4NPF_6 solution in dry acetonitrile with a scan rate of 50 mV/s.

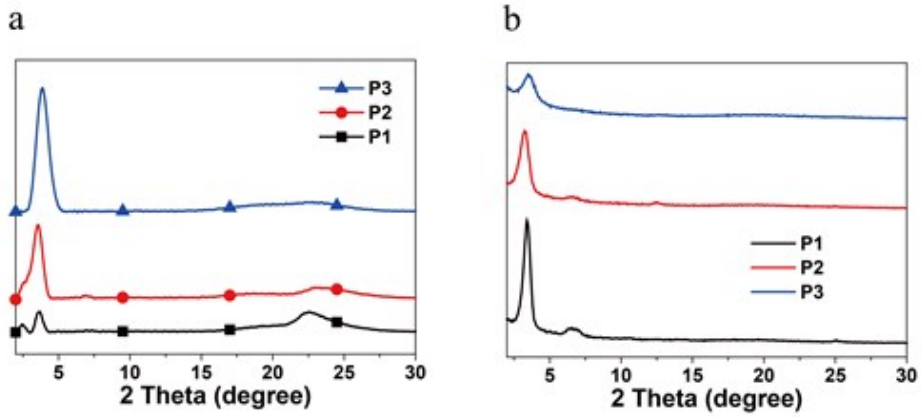


Figure S3. a) Out-of-plane and **b**) in-plane XRD diagrams of the pristine polymer films spin-coated on glass substrate.

4. Characterizations of photodiodes

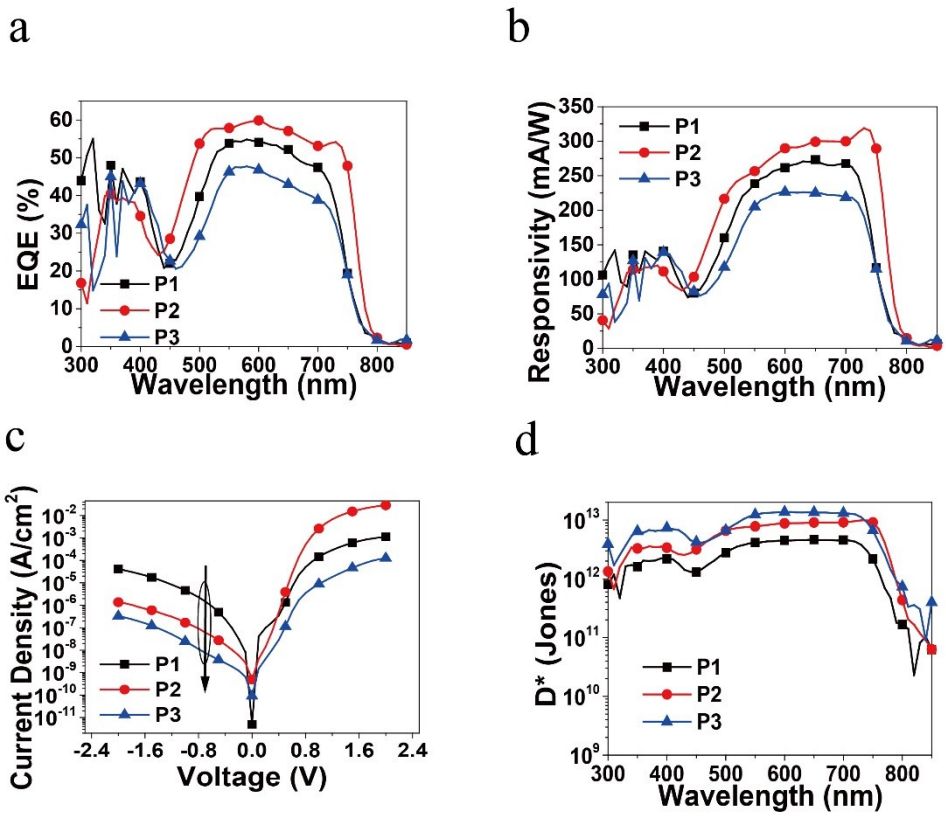


Figure S4. a) EQE (-2 V), **b)** responsivity (-2 V), **c)** *J-V* curves in dark and **d)** specific detectivity (-0.1 V) of photodiodes with the device structure of ITO/PEDOT:PSS/active layers (P1-P3:PTB7-Th) /ZnO/Al and chloroform as solvent.

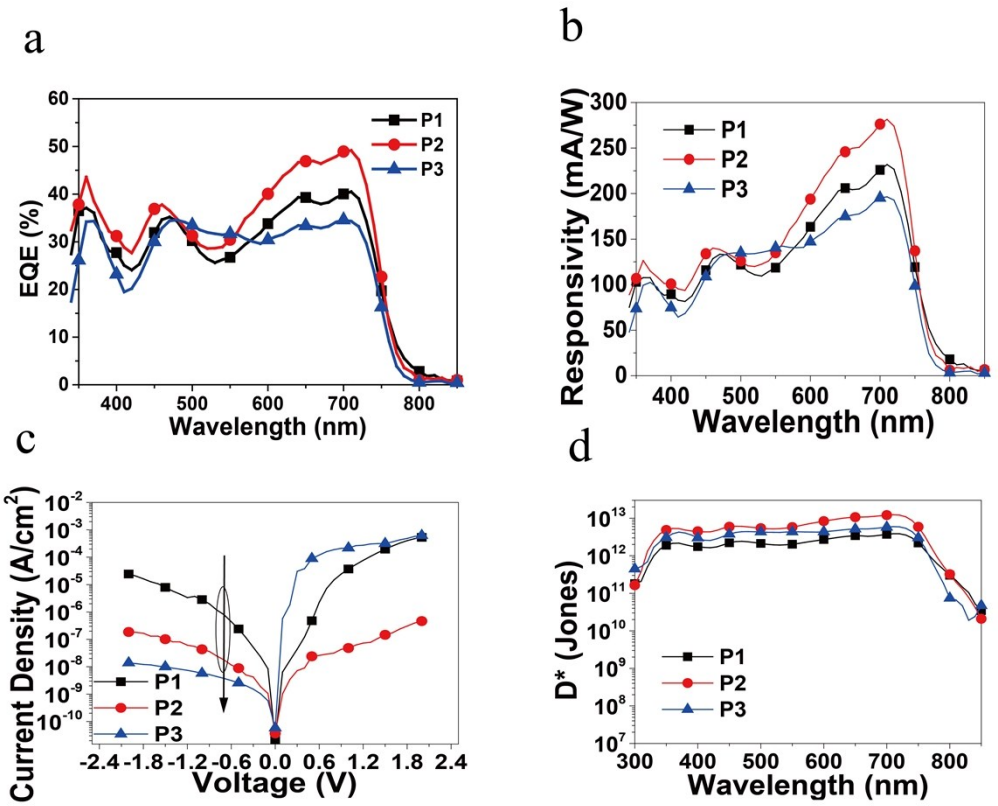


Figure S5. a) EQE (-2 V), **b)** responsivity (-2 V), **c)** *J-V* curves in dark and **d)** specific detectivity (-0.1 V) of photodiodes with the device structure of ITO/PEDOT:PSS/active layers (P1-P3:PTB7-Th) /ZnO/Al and chlorobenzene as solvent.

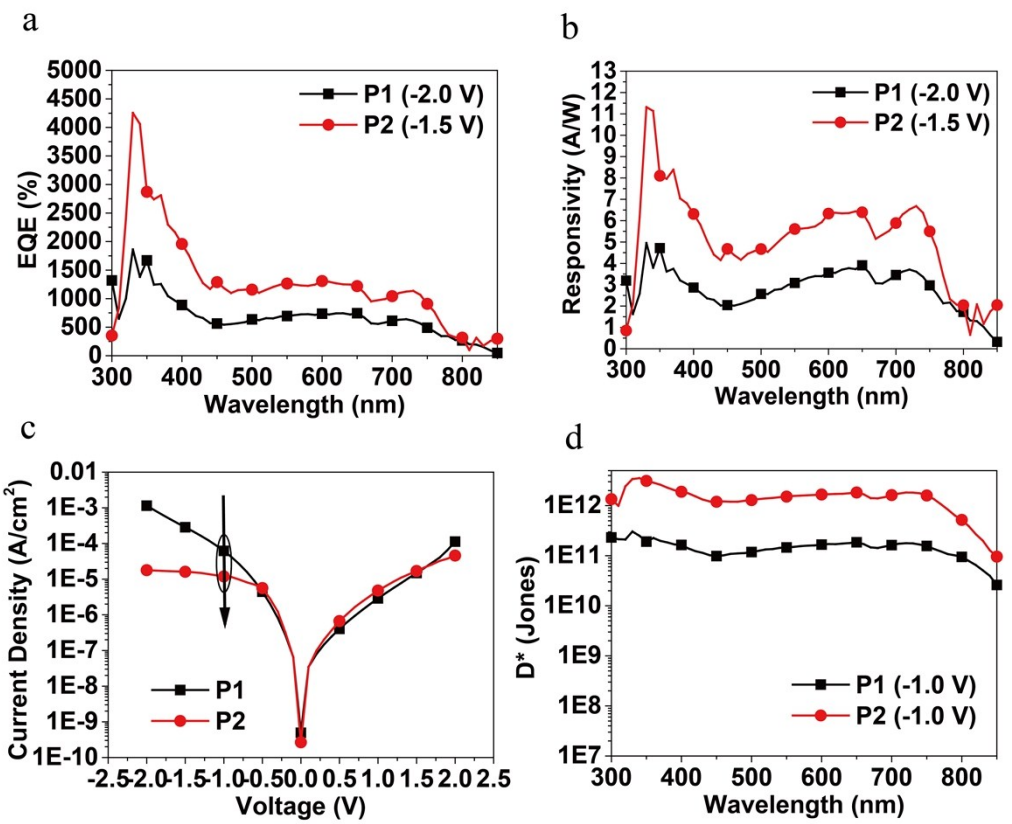


Figure S6. a) EQE (P1 and P2-based devices), **b)** responsivity (P1 and P2-based devices), **c)** *J-V* curves in dark and **d**) specific detectivity of photodiodes (P1 and P2-based devices) with the device structure of ITO/ZnO/active layers (P1-P3:PTB7-Th) /MoO_3/Al and chlorobenzene as solvent.

5. Dark current-voltage characteristics

The dark current-voltage characteristics are described by $J_d=J_0\{\exp[e(V-JR_s)/nk_BT]-1\}$, where J_d is the dark current density, J_0 is the dark saturate current density, V is the applied voltage, n is the ideality factor, k_B is the Boltzmann constant, T is the temperature and e are the electron charge. The fitting method is described in ref. 4 and 5.[4, 5]

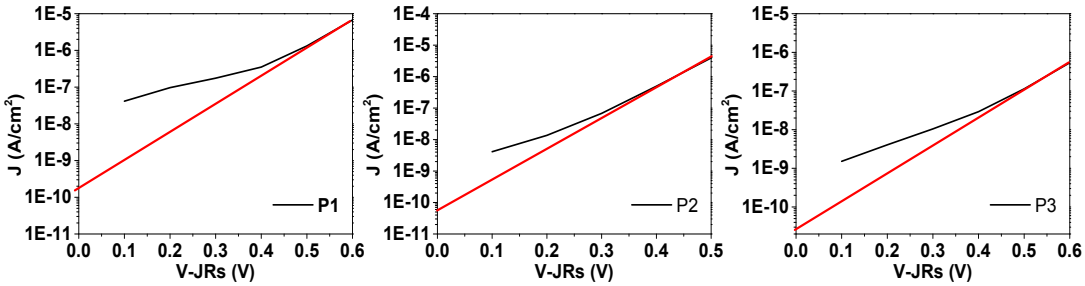

J (A/cm²)
V-JRs (V)
P1
P2
P3

Figure S7. The device structure is ITO/PEDOT:PSS/active layer/ZnO/Al. The original *J-V* curve is shown in Figure S4c. Plot of dV/dJ vs J^{-1} (black line) and linear fitting (red line).

6. References and Notes

[1] Gong, X., Tong, M., Xia, Y., Cai, W., Moon, J. S., Cao, Y., Yu, G., Shieh, C., Nilsson, B., Heeger, A. J. *Science*, **2009**, *325*, 1665.

[2] Yao, Y., Liang, Y., Shrotriya, V., Xiao, S., Yu, L. Yang, Y. *Adv. Mater.* **2007**, *19*, 3979.

[3] Yuan, Z., Fu, B., Thomas, S., Zhang, S., DeLuca, G., Chang, R., Lopez, L., Fares, C., Zhang, G., Bredas, J.-L., Reichmanis, E. *Chem. Mater.* **2016**, *28*, 6045.

[4] Zhang, B., Trinh, M. T., Fowler, B., Ball, M., Xu, Q., Ng, F., Steigerwald, M. L., Zhu, X.-Y., Nuckolls, C., Zhong, Y. *J. Am. Chem. Soc.* **2016**, *138*, 16426.

[5] Dou, L., Yang, Y. M., You, J., Hong, Z., Chang, W. H., Li, G., Yang, Y. *Nat. Commun.* **2014**, *5*, 5404.