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Supporting Information

Broadband organic photodetectors exhibiting photomultiplication with narrow bandgap non-fullerene acceptor as electron trap

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Experimental Section

Device Fabrication: The broadband organic photodetectors with photomultiplication (PM-OPDs) were fabricated on the patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω cm^{-2}. The ITO glass substrates were pre-cleaned by sequential sonication in detergent, deionized water and ethanol. All the cleaned ITO glass substrates were blow-dried by high-purity nitrogen gas and then treated with oxygen plasma for 1 minute to improve its work function and clearance. Subsequently, the poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Clevios P VP AI.4083, purchased from H.C. Starck Co., Ltd.) solution was spin-coated onto the cleaned ITO glass substrates at 5000 rounds per minute (RPM) for 30 s, and then annealed at 150 ℃ for 15 minutes in atmospheric air. After annealing treatment, all the ITO glass substrates coated with PEDOT:PSS layer were transferred into a high-purity nitrogen-filled glovebox to fabricate active layers. Polymer poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione))] (PBDB-T) and 2,2'-((2Z,2'Z)-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-sindaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(4-((2-ethylhexyl)oxy)thiophene-5,2-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (IEICO-4F) (purchased from Solarmer Materials Inc.) were dissolved in chlorobenzene (CB) solvent to prepare 15 mg/mL solutions, respectively. Then, the PBDB-T and IEICO-4F solutions were blended with various volume ratios of 100:1, 100:3, and 100:5, respectively. The mixed solutions were spin-coated onto the top of PEDOT:PSS layer for 30 s and then annealed at 150 ℃ for 10 minutes to prepare active layers. The different thick active layers are fabricated by adjusting the speed of spin-coating. The Al cathode (100 nm) was deposited onto the active layers by thermal evaporation under 5×10^{-5} Pa and the thickness was monitored by using a quartz crystal microbalance. The active area of photodetectors is approximate 3.8 mm^2, which is defined by the vertical overlapping area between Al cathode and ITO anode.

Characterizations and Measurements: The current density *versus* voltage (*J-V*) curves of OPDs were measured by using a Keithley 2400 source meter. The used monochromatic light was provided by a 150 W xenon lamp coupled with a monochromator. The light intensity spectrum of monochromatic light was recorded by using a Thorlabs S120VC power meter. The ultraviolet-visible (UV-Vis) absorption spectra were recorded by a SHIMADZU UV-3101 PC spectrophotometer. The noise current was obtained from the Fourier transform of the dark current *versus* time.

Calculation of performance parameters: The external quantum efficiency (EQE) of OPDs can be calculated according to the ratio of the number of holes collected by electrode to the number of incident photons. Responsivity (*R*) is defined as the ratio of the photo-induced current density to the incident light intensity. The EQE and *R* can be calculated according to Equation **S1** and **S2**:

$$EQE = \frac{(J_L - J_D)/e}{I_{in}/h\nu} \tag{S1}$$

$$R = \frac{J_L - J_D}{I_{in}} = \frac{EQE \cdot e}{h\nu} \tag{S2}$$

in which J_L is the current density under light illumination, J_D is the current density in dark condition, *e* is elementary electron charge (1.6×10^{-19} C), I_{in} is incident light intensity, *h* is the Plank constant, ν is photon frequency.

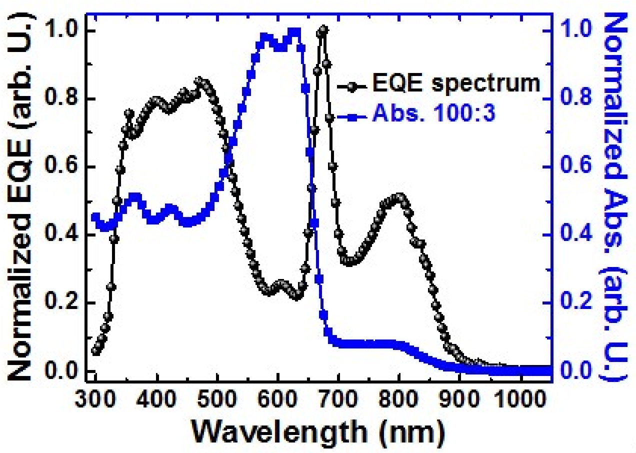

Figure S1. The normalized EQE spectrum of PM-OPDs with PBDB-T:IEICO-4F (100:3, wt/wt) as active layers and the normalized absorption spectrum of PBDB-T:IEICO-4F (100:3, wt/wt) blend thin films.

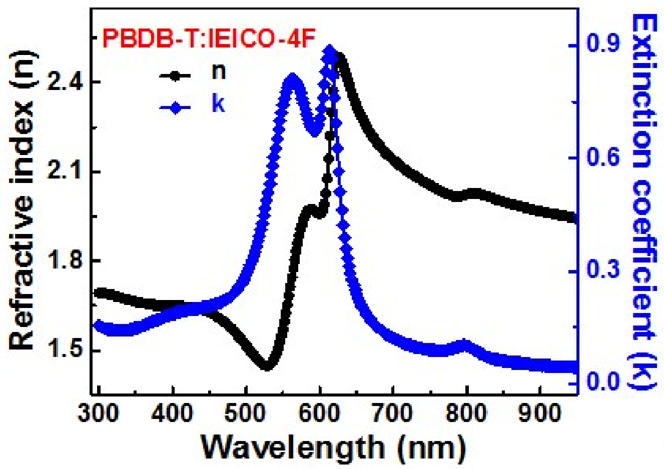

Figure S2. The optical parameters refractive index (n) and extinction coefficient (k) of PBDB-T:IEICO-4F (100:3, wt/wt) blend thin film.

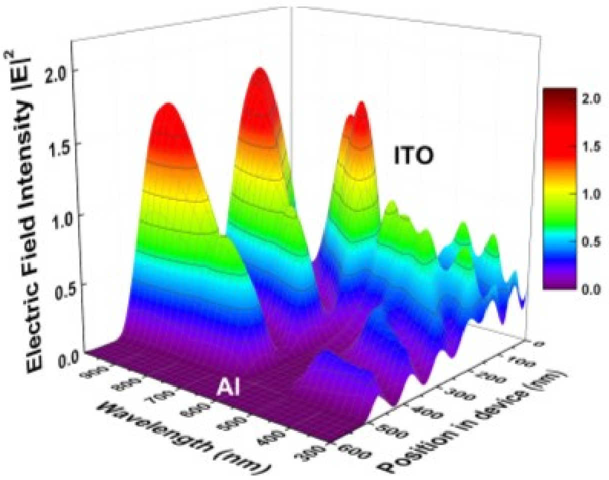

Figure S3. The simulated optical field distribution in the PM-OPDs with the structure of ITO (120 nm)/ PEDOT:PSS (30 nm)/PBDB-T:IEICO-4F (100:3, wt/wt) (350 nm)/Al (100 nm). The position in device axis denotes the distance away from the ITO electrode.

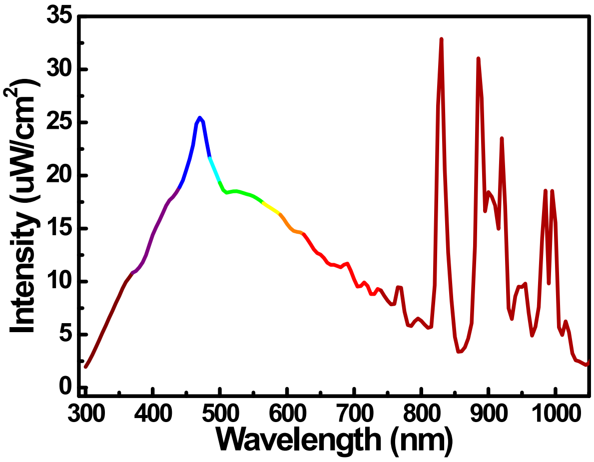

Figure S4. Incident light spectrum of the monochromatic light.

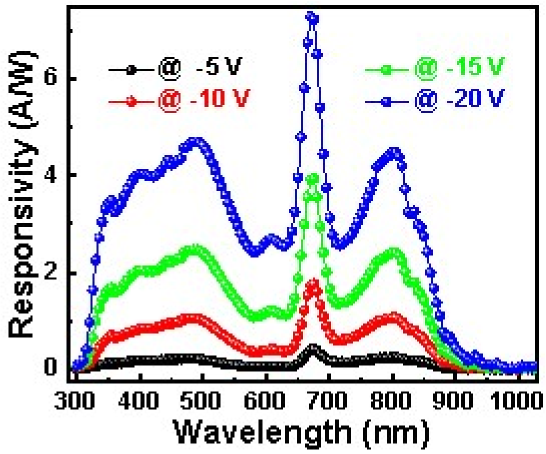

Figure S5. The responsivity spectra of the optimal PM-OPDs with 350 nm PBDB-T:IEICO-4F (100:3, wt/wt) active layers under different reverse biases.

Table S1. The R of the optimal PM-OPDs under different reverse biases.

Voltage / Wavelength	-5V	-10V	-15V	-20V
400nm	0.30	0.93	2.13	4.07
487nm	0.30	1.15	2.51	4.77
581nm	0.15	0.38	1.12	2.46
672nm	0.39	1.75	3.88	7.31
800nm	0.36	1.18	2.48	4.59

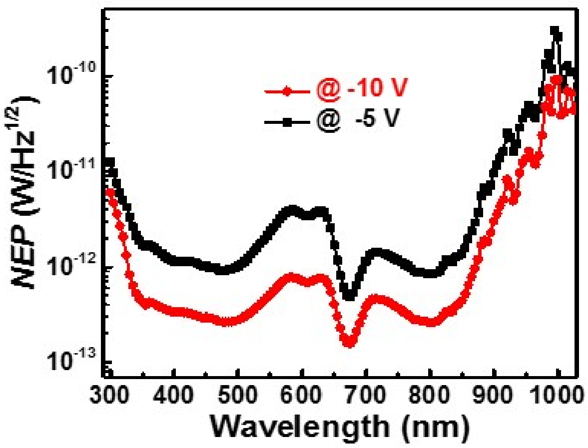

Figure S6. The calculated noise equivalent power (*NEP*) spectrum of the optimal PM-OPDs with PBDB-T:IEICO-4F (100:3, wt/wt) as active layers at -5 V and -10 V.