Supporting Information

Broadband photomultiplication organic photodetectors

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Experimental Section

Device fabrication: The 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 the work function and clearance. Subsequently, the poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Clevios PVP 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 °C 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 10 mg/mL solutions, respectively. Then, the IEICO-4F and PBDB-T solutions were blended with the weight ratios of 1:1 and 3:100, respectively. For the PD-OPDs and single-layered PM-OPDs, the mixed solutions of IEICO-4F:PBDB-T with the weight ratios of 1:1 or 3:100 were individually spin-coated onto the top of PEDOT:PSS layer at 400 RPM for 30 s and then annealed at 150 °C for 10 minutes to prepare active layers. For double-layered PM-OPDs, firstly, the mixed solution of the IEICO-4F:PBDB-T with weight ratio of 1:1 was spin-coated onto the top of PEDOT:PSS layer at 400 RPM for 30 s

and then annealed at 150 °C for 10 minutes to prepare photon harvesting layer; secondly, the mixed solution of the IEICO-4F:PBDB-T with weight ratio of 3:100 were dynamic spin-coated onto the top of IEICO-4F:PBDB-T (1:1, wt/wt) layer at 2000 RPM for 30 s to prepare PM layer. The spin-coating method for preparing organic semiconducting thin films has been commonly reported in many fields, such as organic light emitting diodes, organic solar cells, organic transistors, and organic photodetectors.[1-4] The thickness of active layers were measured by using an AMBIOS Technology XP-2 stylus profilometer. The Al electrode (100 nm) was deposited onto the active layer by thermal evaporation in a high vacuum (10^{-4} Pa) chamber and the thickness was monitored with a quartz crystal microbalance. The active area of the prepared OPDs is approximate 3.8 mm^2, which is defined by the vertical overlapping area between Al electrode and ITO electrode.

Films and Devices Testing: The current density versus voltage (*J-V*) curves of the 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 fast Fourier transform (FFT) of the dark current versus time curves.

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.

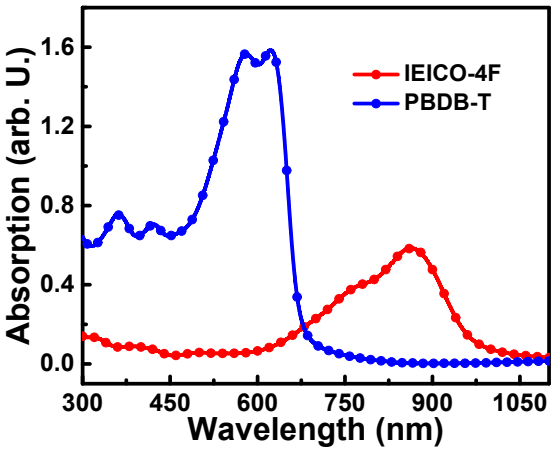

Figure S1 The absorption spectra of neat IEICO-4F and PBDB-T films.

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