

## Supporting Information

### Enhanced Photomultiplication of Organic Photodetectors via Phosphorescent Material Incorporation

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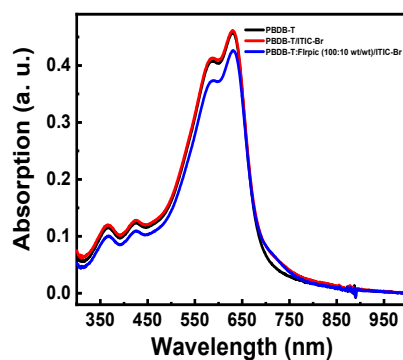
#### Device fabrication

The OPDs were fabricated on the patterned ITO-coated glass substrates (purchased from South China Science and Technology Company) with a sheet resistance of 15  $\Omega/\text{cm}^2$ . 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. The PEDOT:PSS solution was spin-coated on ITO/glass substrates at 5000 rounds per minute for 30 s and then annealed at 150 °C for 15 minutes in atmospheric air. The FIrpic was dissolved in chlorobenzene to prepare 10 mg/ml solutions. The used PBDB-T was dissolved in chlorobenzene to prepare 17 mg/ml solutions. The FIrpic was incorporated into PBDB-T, and the weight ratio of PBDB-T to FIrpic are 100:0, 100:5, 100:10 and 100:15, respectively. The used ITIC-Br was dissolved in dichloromethane and methanol (the volume ratio of dichloromethane to methanol is 4 to 1) to prepare 0.5 mg/ml solutions. The blend solutions consisting of FIrpic and PBDB-T were spin-coated on ITO/PEDOT:PSS substrates at 600 rounds per minute for 30 s and then were directly annealed at 100 °C for 1 minute. The ITIC-Br solution was spin-coated on ITO/PEDOT:PSS/PBDB-T:FIrpic (100:x, wt/wt) substrates at 3000 rounds per minute for 30 s and annealed at 100 °C for 5 minutes. Finally, approximately 100 nm thick Al layer as top electrode was thermally evaporated onto the active layer in a high vacuum ( $10^{-4}$  Pa) chamber. The active area of each

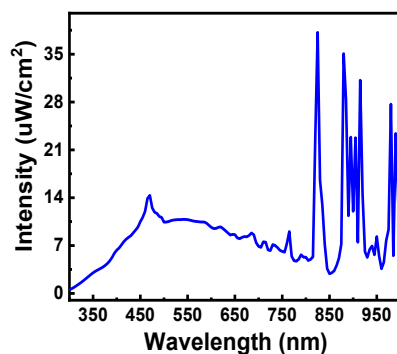
OPDs about 3.8 mm<sup>2</sup> was defined as the vertical overlap of the Al and ITO electrodes.

### Device characterization

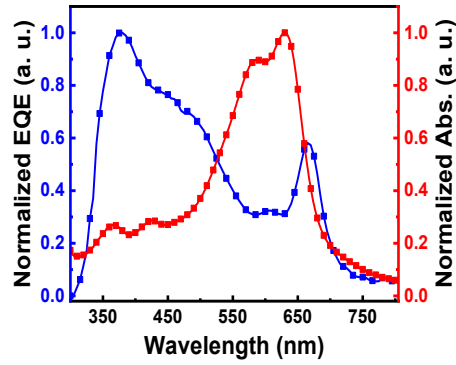
The  $J$ - $V$  curves of all OPDs were measured by using a Keithley 2400 source meter under white light illumination with an intensity of 980  $\mu\text{W}/\text{cm}^2$  and in dark. A monochromatic light could be obtained by the combination of a 150 W Xenon lamp with a monochromator. The monochromatic light intensity spectrum was measured by using a Thorlabs S120VC power meter. The transient photocurrent was measured under the modulation by an electronic shutter and electromagnetic relays. The absorption spectra were obtained by a Shimadzu UV-3101 PC spectrophotometer. The LDR of OPDs was measured by using diode lasers at the wavelength of 660 nm coupled with neutral density filters to manipulate the incident light intensity. Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were accomplished at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea.



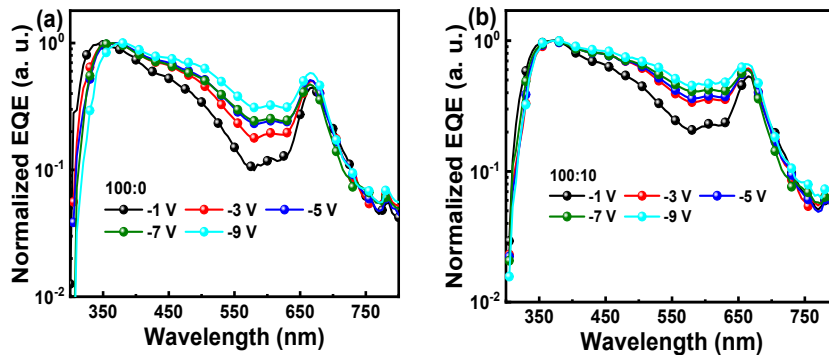
**Figure S1** The absorption spectra of PBDB-T, PBDB-T/ITIC-Br and PBDB-T:Flrpic (100:10, wt/wt)/ITIC-Br films.



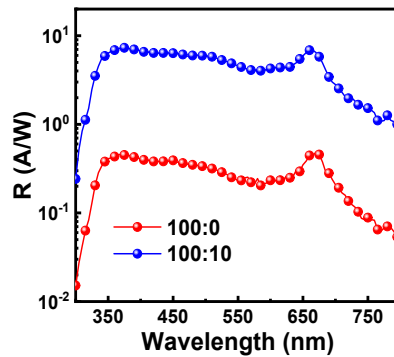
**Figure S2** The incident light intensity spectrum of Xenon lamp.



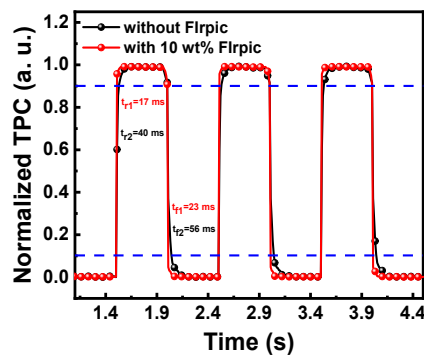
**Figure S3** The normalized EQE spectrum of PM-OPDs with PBDB-T/ITIC-Br layers as active layer under -9 V applied bias and the normalized absorption spectrum of PBDB-T/ITIC-Br blend films.



**Figure S4** The normalized EQE spectra of PM-OPDs (a) without FIrpic and (b) with PBDB-T:FIrpic (100:10, wt/wt) under different reverse bias.



**Figure S5** The responsivity (R) of PM-OPDs without FIrpic or with PBDB-T:FIrpic (100:10, wt/wt) under -9 V bias.



**Figure S6** The transient photocurrent of PM-OPDs under 660 nm light excitation and -9 V bias