Electronic Supplementary Information

Enhancing Performance of Photomultiplication-Type Organic Photodetectors Using Solution-Processed ZnO as an Interfacial Layer

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Device Fabrication: The ITO glass with the resistance≦15 Ω per square was cleaned by ultrasonication using detergent, water, acetone and isopropyl alcohol respectively (30 min each) and then dried in oven at 70 °C overnight. The cleaned ITO glass was treated with UV-O_3 for 15 min. Then, the ZnO precursor solution with a concentration of 0.23 M (zinc acetate dissolving in 2-methoxyethanol mixing with ethanolamine for sufficient stirring) was spin-coated onto the ITO glass at 3000 rpm for 60 s in a N_2-filled glovebox. [S1, S2] The ZnO coated substrates were baked in air at 110 °C for 10 minutes and then annealed at 200 °C for 1 hour. For the comparison, the PEDOT:PSS (purchased from Baytron PAl 4083) was also spin-coated onto the ITO glass at 5000 rpm for 40 s. Then, the PEDOT:PSS coated substrates were baked in air at 120 °C for 10 minute. All the coated substrates were moved into the N_2-filled glovebox. P3HT (purchased from J&K Scientific Ltd.) and O-IDTBR (purchased from Derthon Optoelectronic Materials Science Technology Co. Ltd.) with a weight ratio of 100:1 was dissolved in 1,2-dichlorobenzene (*o*-DCB) to prepare a blended solution with a

concentration of 40 mg/mL. The thick active layers (~255 nm) were formed by spin-coating the active layer solution onto the ZnO- or PEDOT:PSS-coated substrates at 600 rpm for 25 s. Then, the active layers were dried naturally or annealed at 80 °C (20 s or 40 s) immediately. Finally, aluminum electrode (80 nm) was thermally deposited under 10^{-5} Pa. The active layer of all OPDs was 4 mm^2.

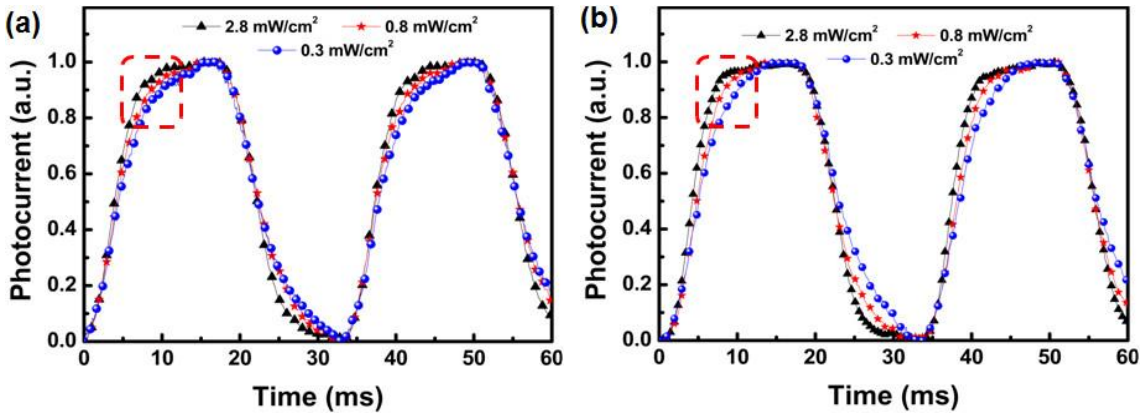

Fig. S1 Transient response characteristics of the OPD under the 525 nm light illumination: under biases of -15 V (a) and 15 V (b). The section circled with red dashed-line shows the gradually shortened rise time of the OPD with increasing light intensity.

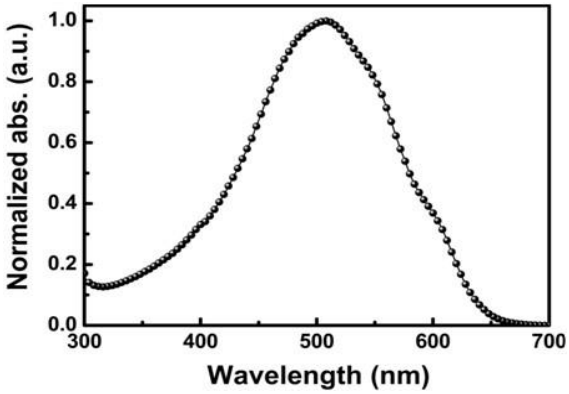

Fig. S2 Normalized absorption spectrum of the active layer annealed at 80 ºC for 20 s.

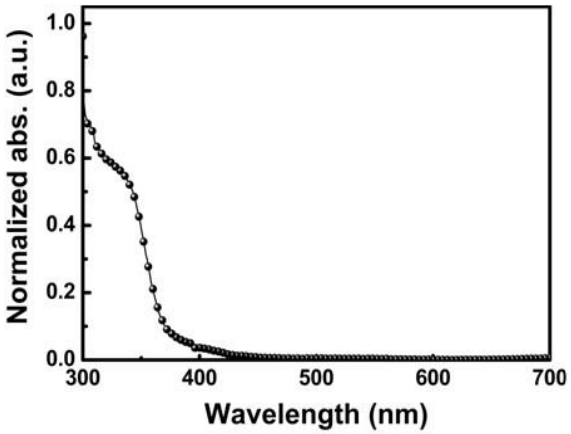

Fig. S3 Normalized absorption spectrum of the ZnO interfacial layer (~40 nm).

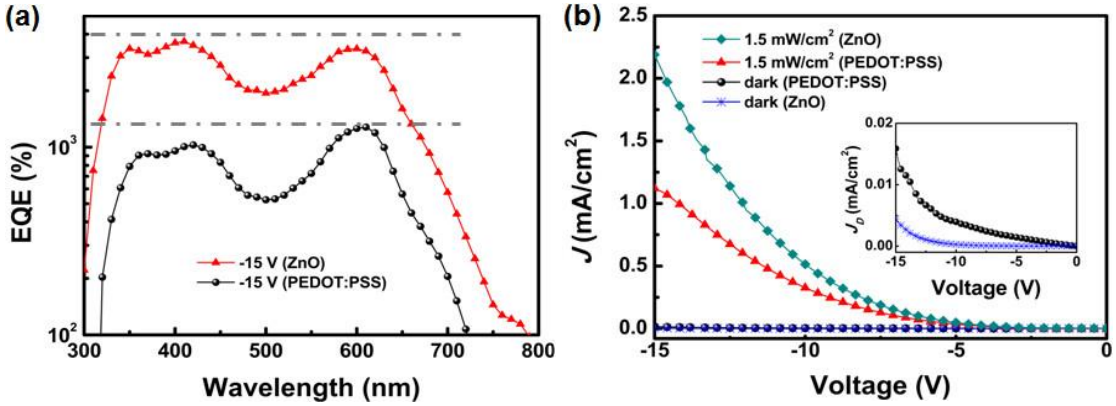

Fig. S4 EQE spectra of the optimized OPD based on ZnO or PEDOT:PSS under -15 V bias (a); Dashed lines in (a) show the clear variation of EQE spectral shapes, especially in the short wavelength range; *J-V* characteristics of the OPD based on ZnO or PEDOT:PSS under dark and light illumination at 1.5 mW/cm^2, respectively (b); The insert in (b) shows the corresponding J_D-*V* characteristics.

References

S1. Z. Yin, Q. Zheng, S.-C. Chen, D. Cai, *ACS Appl. Mater. Interfaces* 2013, **5**, 9015-9025.

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