Supporting information

All-polymer photodetectors with photomultiplication

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Experimental section

The ready-made indium tin oxide (ITO)-coated glass substrates with a sheet resistance of 15 Ω per square were successively cleaned by detergent, deionized water, and ethanol in ultrasonic cleaning and blow-dried with high-purity nitrogen gas. The cleaned ITO substrates were treated by oxygen plasma for 2 min to increase the work function of the ITO and further clean the substrates. The aqueous solution of poly(3, 4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios P VP AI.4083, purchased from H.C. Starck Co., Ltd.) was spin-coated onto the cleaned ITO substrates at a spin speed of 5000 rounds per minute (rpm) for 30 s and the PEDOT:PSS/ITO substrates were annealed at 150 °C for 15 min in the atmosphere. Then the processed ITO substrates were transferred to a high-purity nitrogen-filled glove-box. The polymer poly(3-hexylthiophene) (P3HT) (purchased from Solarmer Materials Inc.) and PZ1 (purchased from Solarmer Materials Inc.) were dissolved in 1,2-dichlorobenzene (*o*-DCB) and chlorobenzene (CB) to prepare 40 mg/mL and 10 mg/mL solutions, respectively. The incorporation weight ratios of P3HT:PZ1 are 100:1, 100:2, 100:3, 100:4, and 100:5. The mixed solution was spin-coated onto the PEDOT:PSS-coated ITO substrates at 800 rpm for 30 s to prepare the active layers. A series of active layers based on P3HT:PZ1 with weight ratio of 100:4 were prepared

to undergo different self-assembly time (0.5, 5, and 10 min). Then the active layers were annealed at 100 °C for 1 min. And the reference active layers were dried naturally. Finally, the 100 nm aluminum (Al) layers acting as electrodes were formed on the active layers by thermal evaporation in a high vacuum (10^{-4} pa) chamber. The active area of each PM type OPDs is about 3.8 mm^2 defined as the vertical overlap of the Al and ITO electrodes.

The current density versus voltage (*J-V*) curves of all the PM type all-PPDs were measured by Keithley 2400 source meter in dark and under white light illumination with the intensity of 8.2 mW/cm^2. The wavelength of incident light provided by a 150 W xenon lamp coupled with a monochromator was scanned from 300 nm to 800 nm. All measurements were carried out in the high-purity nitrogen-filled glove-box. The absorption spectra were obtained by a Shimadzu UV-3101 PC spectrophotometer. The optical constants (refractive index *n* and extinction coefficients *k*) of used materials were measured by a SE200BM-M100 spectroscopic ellipsometer. Grazing incidence X-ray diffraction (GIXD) images were obtained by a five-circle Huber diffractometer at Beijing Synchrotron Radiation Facility (BSRF). A bent-triangle silicon crystal was used to select the X-rays of a wavelength of 1.5476 Å. GIXD peak intensity was increased by choosing a grazing incidence angle of 0.4° to investigate the crystallinity and orientation prevailed throughout the film. The noise current was obtained from the Fourier transform of the dark current versus time. The transient photocurrent was measured under the modulation by an electronic shutter and electromagnetic relays.

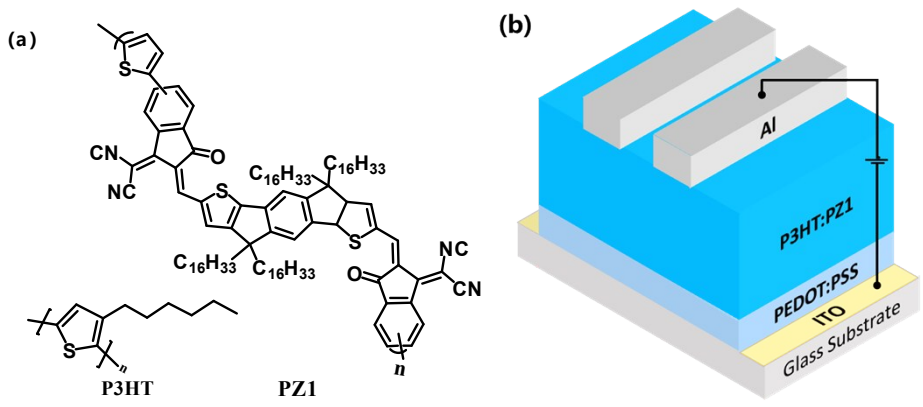

Fig. S1 (a) Molecular structures of P3HT and PZ1. (b) Structure schematic diagram of PM type

all-PPDs.

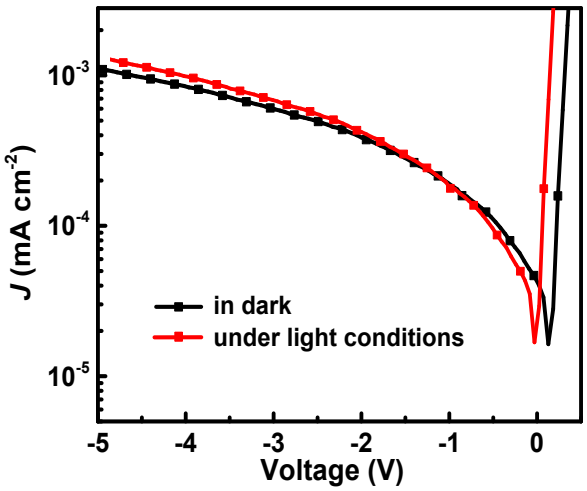

Fig. S2 The *J-V* curves of device with a structure of ITO/PEDOT:PSS/P3HT/Al in dark and under white light illumination with an intensity of 8.2 mW cm^{-2} at -5 V bias.

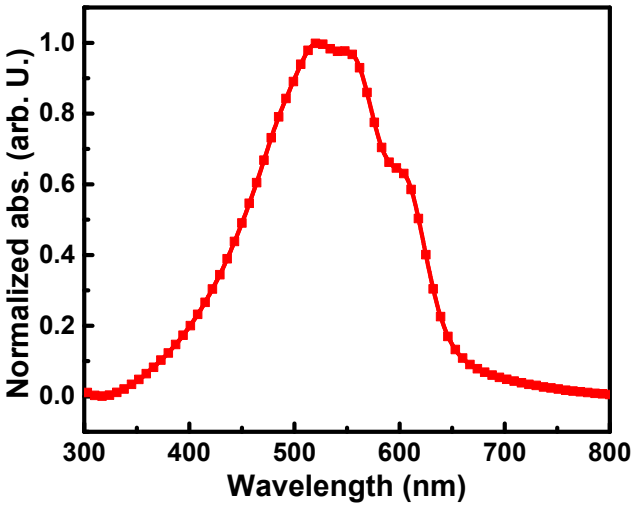

Fig. S3 Normalized absorption spectrum of neat P3HT films.

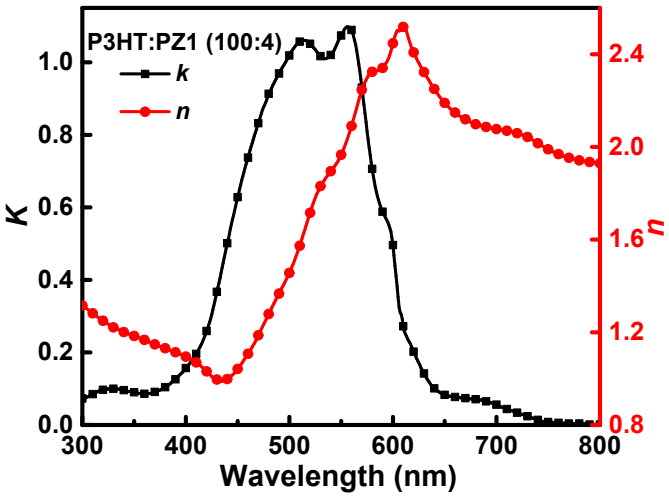

Fig. S4 Extinction coefficient *k* and refractive index *n* of the blend film P3HT:PZ1 (100:4, wt/wt).

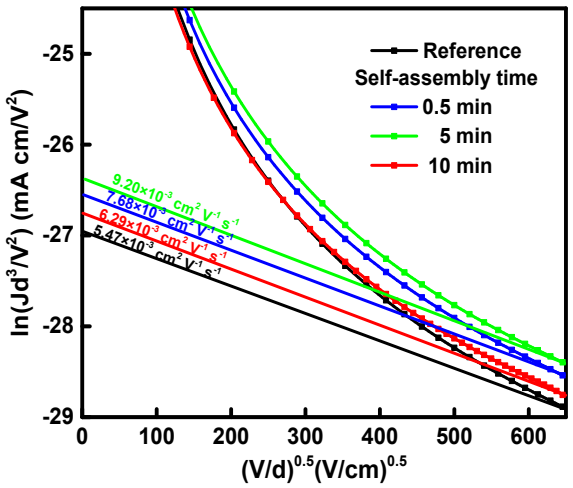

Fig. S5 The $\ln(Jd^3/V^2)$ versus $(V/d)^{0.5}$ curves and hole mobility of the hole-only devices with the active layers undergoing different self-assembly time.

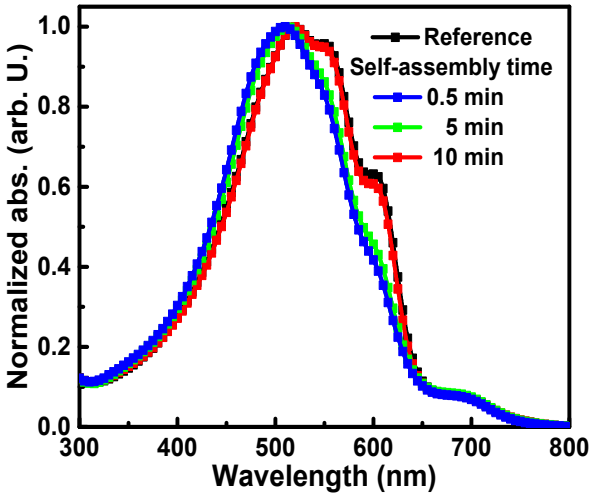

Fig. S6 Normalized absorption spectra of the blend films with different self-assembly time.

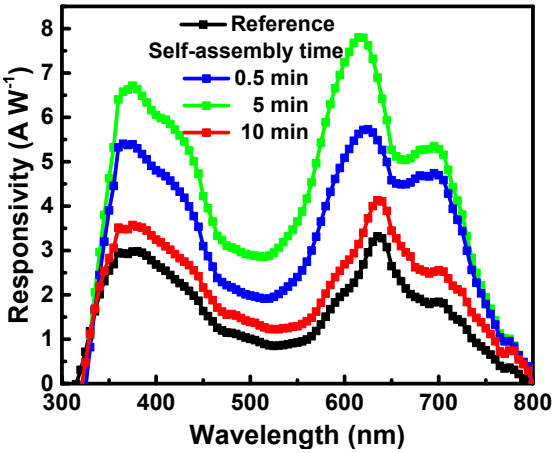

Fig. S7 Responsivity of the PM type all-PPDs with different self-assembly time at -5 V bias.

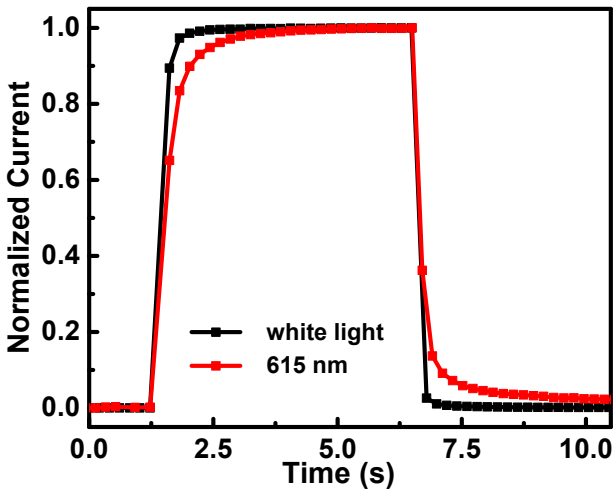

Fig. S8 Transient photocurrent curves of the optimized PM type all-PPDs under white light illumination with light intensity of 8.2 mW cm^{-2} and 615 nm light illumination with light intensity of 1.5 mW cm^{-2} at -5 V bias.