Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information of "Revealing the working mechanism of polymer photodetectors with ultra-high external quantum efficiency"

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The photogenerated electron volume density in the active layer is estimated according to:

$$\rho(\lambda) \propto |E(\lambda)|^2 \times \eta_A(\lambda) \times \eta_D$$

Here, $\rho(\lambda)$ is the electron volume density in each small region, $|E(\lambda)|^2$ is the optical field intensity, $\eta_A(\lambda)$ is the absorption coefficient, and η_D is the electron dissociation coefficient. The distribution of P3HT and $PC_{71}BM$ in the blend films can be considered homogeneous due to the good miscibility of P3HT and $PC_{71}BM$.[1, 2] Therefore, η_D is constant in the whole bulk film. The photogenerated electron volume density can be estimated by:

$$\rho(\lambda) \propto |E(\lambda)|^2 \times \eta_A(\lambda)$$

Considering the homogeneous distribution of P3HT and $PC_{71}BM$ in the blend films, the $\eta_A(\lambda)$ is also constant in the whole bulk film for the same incident light wavelength. Therefore, the normalized photogenerated electron distribution can be estimated according to the optical field distribution and the absorption spectrum of the bulk film. The $|E(\lambda)|^2$ of the PM type PPDs and confirmatory devices was calculated by using the program reported by Yuan Li,[3-5] as shown in **Fig. S1**. This calculation was carried out using transfer matrix method (TMM), which was commonly

used in optical field distribution analysis for organic photodetectors and organic solar cells.[6, 7]

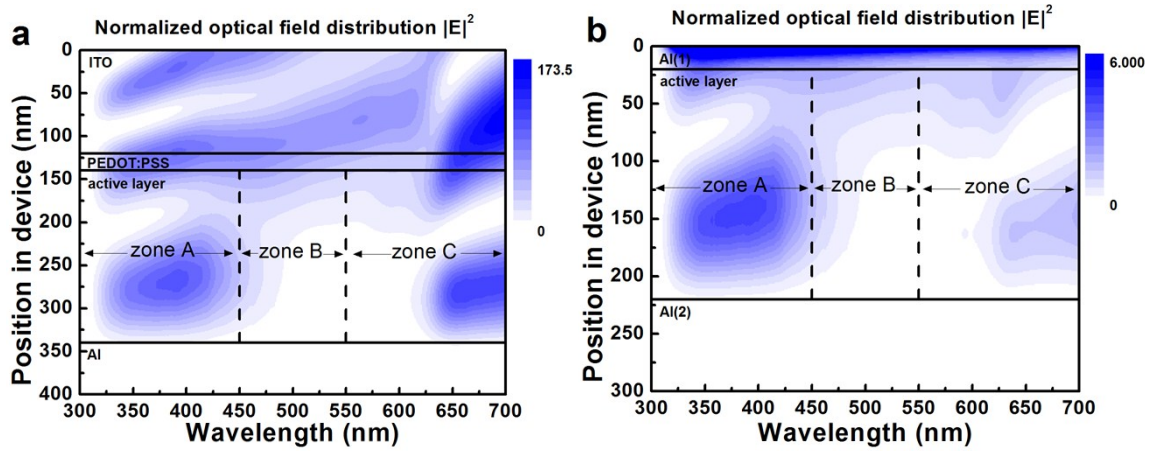

Fig. S1. Normalized optical field distribution. (a) PM type PPDs; (b) confirmatory devices.

The EQE spectra of confirmatory devices under different reverse bias are shown in **Fig. S2a**. The EQE spectral shape of confirmatory devices under reverse bias is similar to the PPDs; however, the EQE values of confirmatory devices are much lower than those of the PPDs under the same bias condition. It should be attributed to the low transmittance (< 6% from 300 nm to 700 nm) of the glass substrate coated by Al(1) layer, comparing with the high transmittance (usually > 80%) of glass substrate with 120 nm ITO layer, as shown in **Fig. S2b**.

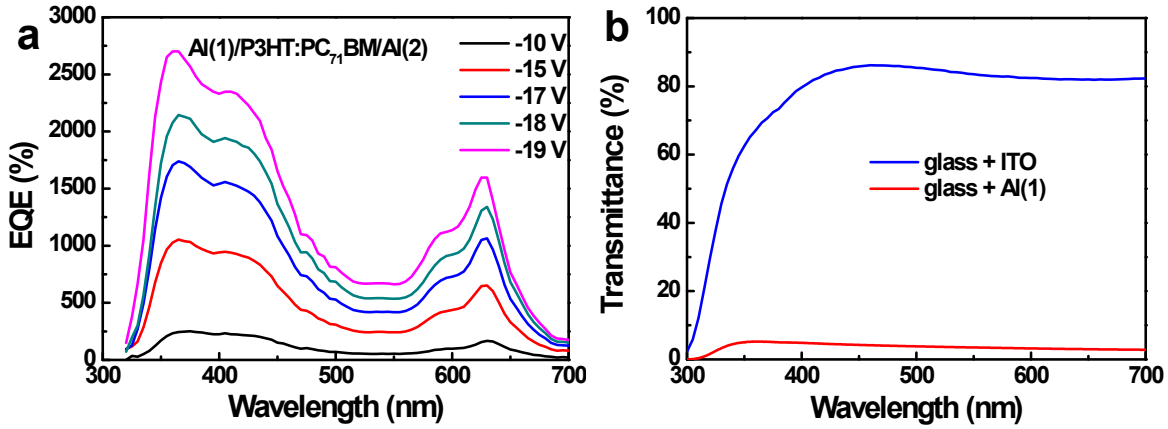

Fig. S2. (a) The EQE spectra of confirmatory devices under different reverse bias. (b) Transmittance spectrum of glass substrate coated by 20 nm A(1) layer or 120 nm ITO layer.

Transient J_{ph} curves of confirmatory devices under different light illumination and bias conditions are shown in **Fig. S3**. The saturated J_{ph} values under different light illumination well accords with the EQE spectra of the confirmatory devices under the same bias.

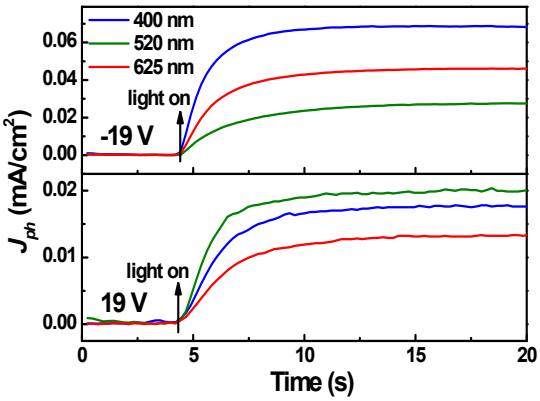

Fig. S3. Transient J_{ph} curves of confirmatory devices under 400 nm, 520 nm or 625 nm light illumination and 19 V or -19 V bias.

The monochromatic light used in all measurements was provided by a 150 W xenon lamp coupled with a monochromator. Light intensity spectrum of the monochromatic lights through a monochromator was measured and is shown in **Fig. S4.**

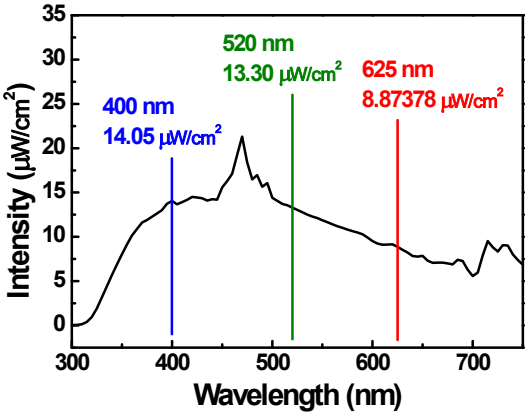

Fig. S4. Light intensity spectrum of the monochromatic lights through a monochromator.

The increased EQE values along with the increase of bias can be well explained from the following sections: i) the mechanism of PM type photodetectors is attributed to trap-assisted hole tunneling injection, the hole tunneling injection should be enhanced along with the reverse bias. ii) the transport of injected holes in the active layer can be improved under the higher electric filed along with the increase of applied bias. The phenomenon can be well explained by following equation:

$$\mathrm{EQE} = \frac{\chi\tau}{T} = \frac{\chi\tau\mu V}{L^2}$$

where χ is the fraction of excitons that dissociated into trapped electrons and free holes, τ is the lifetime of trapped electron, T is the hole transport time, V is the applied bias, L is the active layer thickness, and μ is the field dependent hole carrier mobility. It is apparent that the hole transport time (T) of passing through the whole active layer should be deceased under the higher applied bias, resulting in the increase of EQE values.

Therefore, the enhanced hole tunneling injection and the improved hole transport in the active layer result in the increased EQE values along with the increase of bias.

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