Supporting Information

Photomultiplication type organic photodetectors based on electron tunneling injection

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Experimental Section:

Materials: Polymer poly(3-hexylthiophene) (P3HT) was purchased from Organtec Material Inc. and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) was purchased from Luminescence Technology Corp. The molecular weight and regioregularity of used P3HT are about 50,000 g/mol and 91%-94%, respectively. Zinc acetate dihydrate was purchased from Sigma–Aldrich. All products were used as received.

Device Fabrication: The organic photodetectors used here were fabricated on indium tin oxide (ITO) glass substrates with a sheet resistance of 15 Ω per square. The ITO glass substrates were rinsed with standard procedure, subsequently were dried by utilizing pure nitrogen gas and treated by oxygen plasma lasted 1 min for improving its clearance and work function. Then, all the cleaned ITO glass substrates were transferred into a high-purity nitrogen-filled glove box. Zinc acetate dihydrate was dissolved in 2-methoxyethanol (adding 2.8% v/v of ethanolamine) to prepare 102 mg/ml solution. The zinc acetate dihydrate solution

was spin-coated on ITO substrates at 4000 rounds per minute for 30 seconds in high-purity nitrogen-filled glove box to avoid the reaction between zinc acetate dihydrate and oxygen for obtaining homogeneous zinc acetate dihydrate films. Then, the substrates with zinc acetate dihydrate films were annealed in air to obtain ZnO films. Organic materials P3HT and PC$_{71}$BM were dissolved in organic solvent 1,2-dichlorobenzene (o-DCB) to prepare 30 mg/ml solution with different weight doping ratio of PC$_{71}$BM:P3HT (100:5, wt/wt). The mixed solution was drop-coated on the top of ZnO layer to prepare different thick active layers and then the wet active layers were directly dried at 100 °C for 10 minutes. Under 10^{-4} Pa condition in vacuum chamber, 80 nm Au film was finally deposited onto the active layers based on the thermal evaporation method and the film thickness was monitored by utilizing a quartz crystal microbalance. The active area of the OPDs is defined by the vertical overlap of ITO and Au electrode, approximate 3.8 mm^2 in this study.

Characterizations and Measurements: Current versus voltage (*I-V*) curves of the OPDs was recorded by using a Keithley-2400 source meter. A monochromatic light can be obtained by the combination of a 150 W xenon lamp with a monochromator. The monochromatic light intensity spectrum was measured by utilizing a Thorlabs S120VC power meter. All measurements were carried out in glove box filled high-purity nitrogen. The UV-visible absorption spectra were recorded by a SHIMADZU UV-3101 PC spectrophotometer. The active layer thickness was measured using an AMBIOS Technology XP-2 stylus profilometer. The refractive index *n* and extinction coefficients *k* of used materials were measured by a SE200BM-M100 spectroscopic ellipsometer. The LDR of the OPDs was measured under monochromatic light of 650 nm generated by diode laser. The incident light intensity was manipulated by utilizing different neutral density filters.

Photogenerated hole distribution calculation:

Photogenerated hole density in the active layers can be estimated according to:

$$\rho(\lambda) \propto \frac{\left|E(\lambda)\right|^2}{h\nu} \times \alpha(\lambda) \times \eta_D \qquad \text{(S1)}$$

Here, $\rho(\lambda)$ is the photogenerated hole density, $|E(\lambda)|^2$ is the optical field intensity, which is calculated using Transfer Matrix method. $\alpha(\lambda)$ is the absorption coefficient, and η_D is the exciton dissociation coefficient. The distributions of P3HT and $PC_{71}BM$ in the blend films are considerably homogeneous due to the good miscibility of P3HT and $PC_{71}BM$ in 1,2-dichlorobenzene (o-DCB).[1,2] Therefore, the η_D can be considered as constant in the entire active layers. On the basis of above analysis, photogenerated hole density can be estimated by the following equation:

$$\rho(\lambda) \propto \frac{\left|E(\lambda)\right|^2}{h\nu} \times \alpha(\lambda) \qquad \text{(S2)}$$

Considering the homogeneous distribution of P3HT and $PC_{71}BM$ in the active layers, $\alpha(\lambda)$ is also constant in the whole active layers for the same incident light wavelength. Therefore, the photogenerated hole distribution can be estimated according to the optical field distribution in the active layer. The $|E(\lambda)|^2$ in the active layer of OPDs was calculated using Transfer Matrix method.

Transfer Matrix calculation:[3,4]

Light is considered as a plane wave in transfer matrix theory. Only the light incident perpendicular to the substrate will be considered for OPDs devices. The optical field at any point in the device is a complex quantity and is given a positive superscript $E^+(x)$ for waves traveling from left to right and a negative superscript $E^-(x)$ for waves traveling from right to left, as shown in **Scheme 1**. The device are stacked of m layers, each of which is

described by its complex index of refraction $\tilde{n} = n + i\kappa$ and thickness d, sandwiched between the glass substrate and the atmosphere. The behavior of light at the interface between two layers, j and k, can be described by a 2×2 matrix that contains the complex Fresnel coefficients. This matrix $\mathbf{I}_{jk}$ is known as the interface matrix, which for normal incidence can be given as:

$$I_{ij} = \begin{bmatrix} (\tilde{n}_j + \tilde{n}_k)/2\tilde{n}_j & (\tilde{n}_j - \tilde{n}_k)/2\tilde{n}_j \\ (\tilde{n}_j - \tilde{n}_k)/2\tilde{n}_j & (\tilde{n}_j + \tilde{n}_k)/2\tilde{n}_j \end{bmatrix} \tag{S3}$$

Similarly, the effect on the optical field from propagating through each layer is described by a 2×2 matrix $\mathbf{L}_j$ known as the layer matrix:

$$I_{ij} = \begin{bmatrix} e^{-i\xi_j d_j} & 0 \\ 0 & e^{i\xi_j d_j} \end{bmatrix} \tag{S4}$$

where $\xi_j = 2\pi\tilde{n}_j / \lambda$ and λ is the wavelength of the light. The components of the optical field within the substrate (subscript 0) are related to those in the atmosphere (subscript m+1) by the total transfer matrix $\mathbf{S}$:

$$\begin{bmatrix} E_0^+ \\ E_0^- \end{bmatrix} = S \begin{bmatrix} E_{m+1}^+ \\ E_{m+1}^- \end{bmatrix} \tag{S5}$$

where $\mathbf{S}$ is the product of all interface and layer matrices

$$S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} = \left(\prod_{v=1}^{m} I_{(v-1)v} L_v \right) I_{m(m+1)} \tag{S6}$$

The field quantities in Eq. (S5) are those that exist at the boundaries with the stack of m layers that makes up the active part of the device. Considering light incident from the substrate side only requires that $E_{m+1}^- = 0$, allowing the reflection and transmission coefficients of the multilayer stack to be expressed as

$$r = S_{21}/S_{11} \tag{S7a}$$
$$t = 1/S_{11} \tag{S7b}$$

To determine the optical field at a distance x within layer j of the device, one must add the left- and right-traveling waves,

$$E_j(x) = E_j^+(x) + E_j^-(x) \tag{S8}$$

To find these two latter quantities, Eq. (S6) is split into two partial transfer matrices by the relation $S = S_j' L_j S_j''$. These two matrices are separately defined as

$$S_j' = \begin{bmatrix} S'_{j11} & S'_{j12} \\ S'_{j21} & S'_{j22} \end{bmatrix} = \left(\prod_{v=1}^{j-1} I_{(v-1)v} L_v \right) I_{m(m+1)}, \tag{S9a}$$

$$S_j'' = \begin{bmatrix} S''_{j11} & S''_{j12} \\ S''_{j21} & S''_{j22} \end{bmatrix} = \left(\prod_{v=j+1}^{m} I_{(v-1)v} L_v \right) I_{m(m+1)} \tag{S9b}$$

Algebraic manipulation then allows Eq. (S8) to be expressed in terms of known quantities,

$$E_j(x) = t_j^+ \left[e^{i\xi_j x} + r_j'' e^{i\xi_j(2d_j - x)} \right] E_0^+ \tag{S10}$$

where E_0^+ is the optical field inside the substrate incident on layer 1,

$$t_j^+ = \left[S'_{j11} + S'_{j12} r_j'' e^{2i\xi_j d_j} \right]^{-1} \tag{S11}$$

And

$$r_j^+ = S''_{j21} / S''_{j11} \tag{S12}$$

The substrate cannot be included directly in the transfer-matrix calculation due to the large thickness of the glass ~ (1.0 mm). However, to obtain quantitatively accurate results for the intensity in each layer, the effect of the substrate is included by summing the intensities within the glass as opposed to the optical fields. The intensity of light incident on the multilayer from within the substrate I_S is then given by

$$I_S = I_0 \frac{T_S e^{-\alpha_S d_S}}{1 - R R_S e^{-2\alpha_S d_S}} = I_0 T_{\text{int}} \tag{S13}$$

where I_0 is the light intensity incident on the device, R and T are the reflectance and transmittance of the multilayer stack, and variables subscripted with S represent values for the

substrate. This allows us to define an internal transmittance T_{int} for the substrate in terms of the absorption coefficient $\alpha_j = 4\pi\kappa_j / \lambda$. By using Eq. (S10) and Eq. (S13), the light intensity at a distance x within layer j of the device can be expressed as

$$I_j(x) = I_0 T_{int} \left| t_j^+ \right|^2 \mathrm{Re}\left(\frac{\tilde{n}_j}{\tilde{n}_s} \right) \left\{ e^{-\alpha_j x} + \rho_j^{"2} e^{-\alpha_j(2d_j - x)} + 2\rho_j^{"} e^{-\alpha_j d_j} \cos\left[4\pi n_j (d_j - x)/\lambda + \delta_j^{"} \right] \right\} \quad (S14)$$

where $\rho_j^{"}$ is the argument and $\delta_j^{"}$ is the phase of the quantity in Eq. (S12). The optical field intensity at every point in the device can be calculated by Eq. (S14).
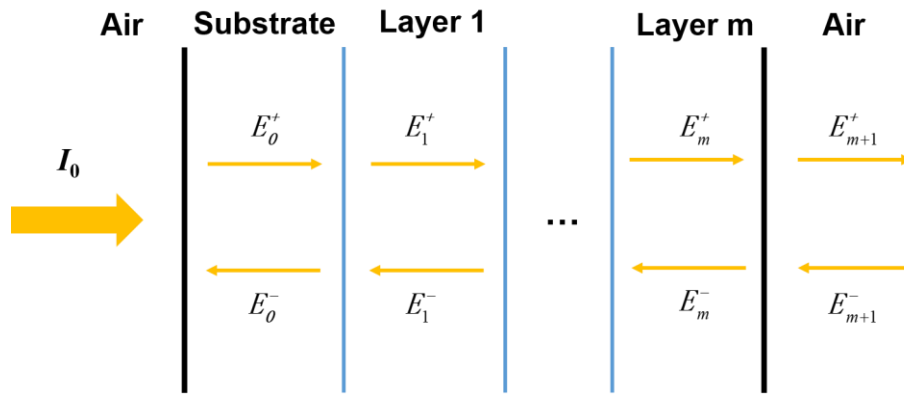
Scheme 1. Schematic diagram of incident light transmission in the device consisting of a stack of m layers.
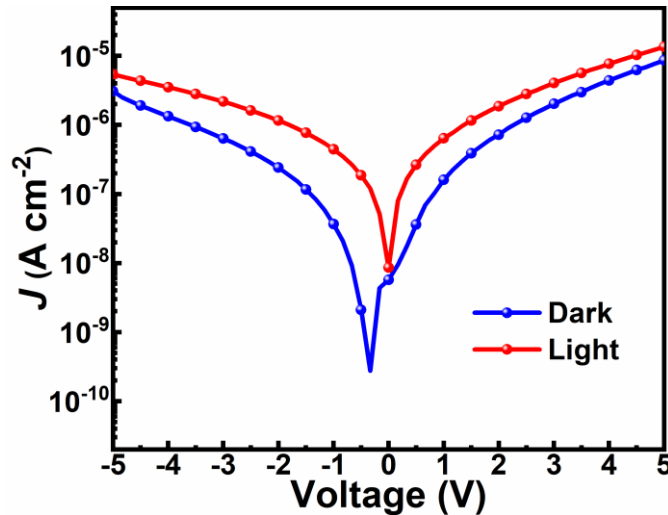
Figure S1. The *J-V* curves of ITO/ZnO/PC$_{71}$BM/Au device in dark and under white light illumination with an intensity of 2 mW cm^{-2}.

The *J-V* curves of ITO/ZnO/PC$_{71}$BM/Au device were measured in dark and under white

light illumination with an intensity of 2 mW cm^{-2}, as shown in **Figure S1**. It is apparent that the *J-V* curves of the special OPDs almost overlap in dark and under light illumination conditions, indicating no any photo-response in the special OPDs. According to the *J-V* curves of OPDs with PC$_{71}$BM orPC$_{71}$BM:P3HT (100:5, wt/wt) as active layers, the isolated P3HT in active layers should play vital role as hole traps in inducing interfacial band bending for efficient electron tunneling injection under light illumination condition.
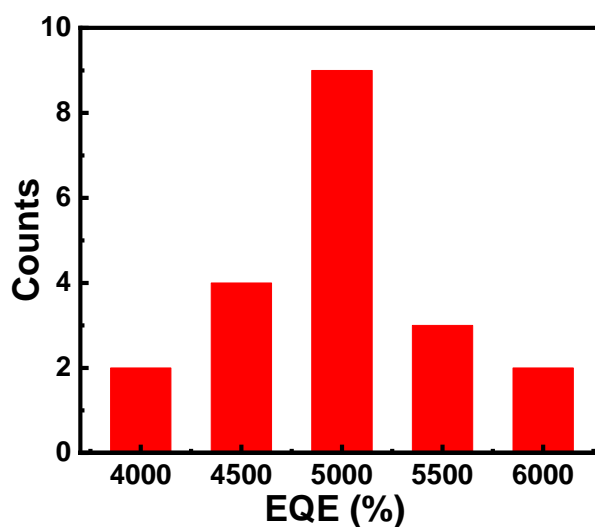
Figure S2. The statistical EQE at 640 nm distribution histogram of 20 individual PM type OPDs under -5 V bias.
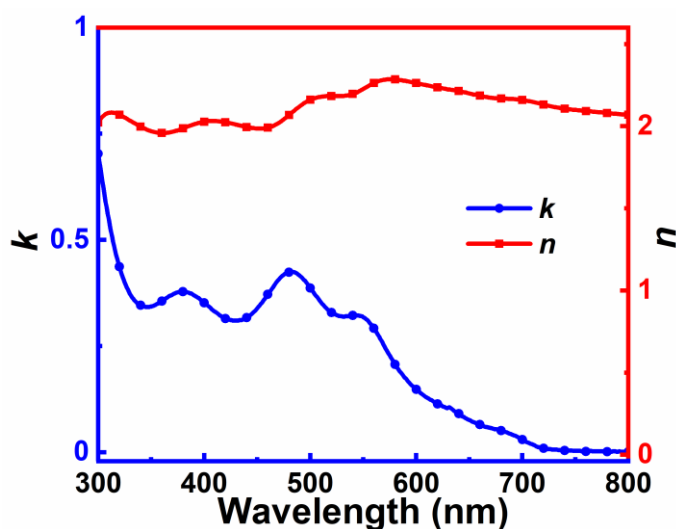
Figure S3. Optical constants (refractive index *n* and extinction coefficient *k*) of PC$_{71}$BM:P3HT (100:5, wt/wt) films.
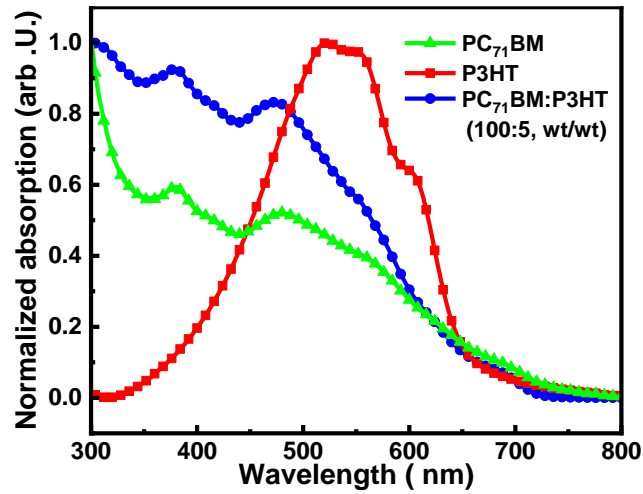
Figure S4. The normalized absorption spectra of PC$_{71}$BM, P3HT and their blend films.
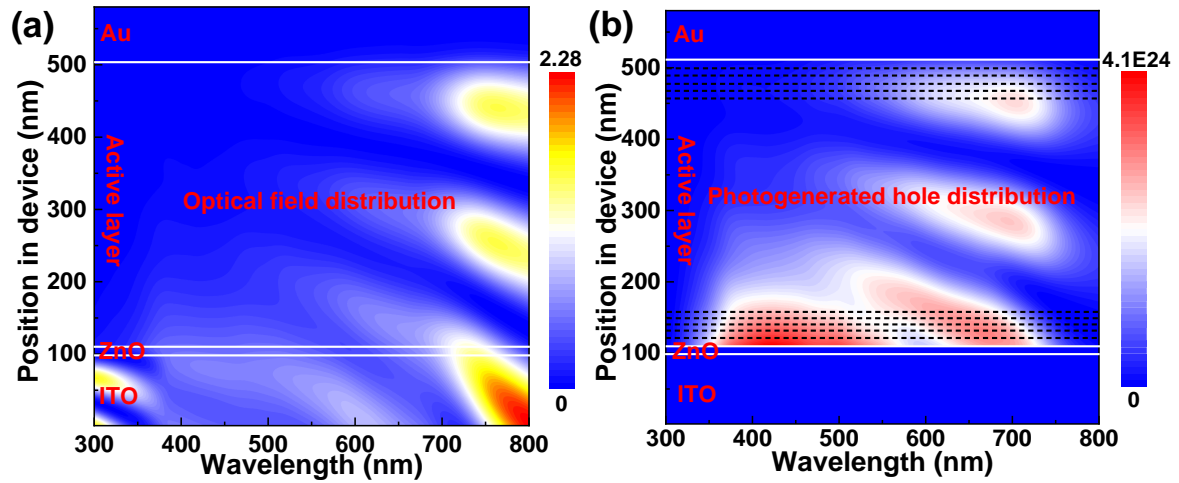

Figure S5. The two-dimension color map of the optical field distribution in the PM type OPDs and photogenerated hole distribution in the active layers. (a) Optical field distribution. (b) Photogenerated hole distribution.
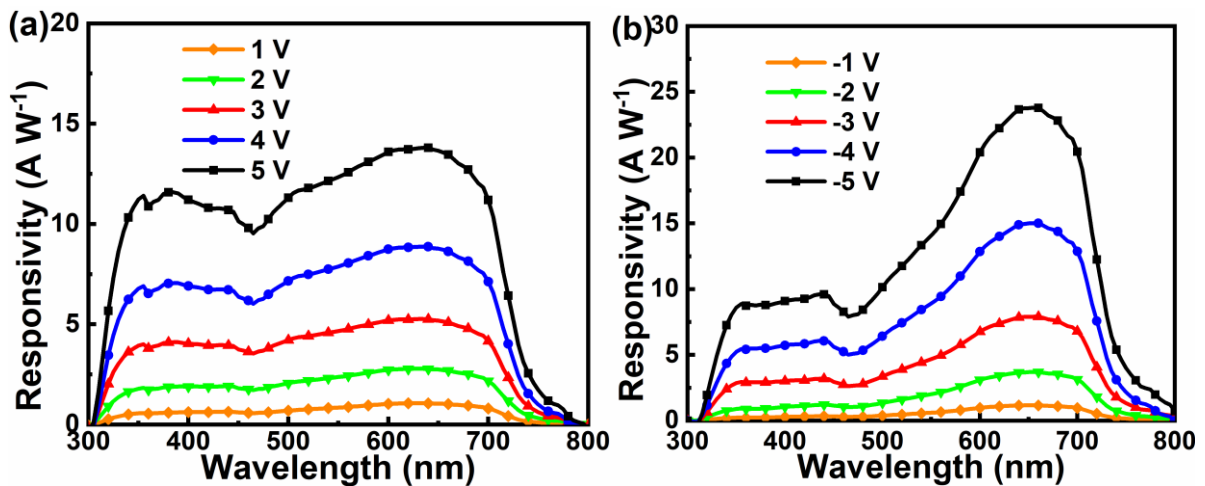

Figure S6. The responsivity spectra of the PM type OPDs under different forward and reverse
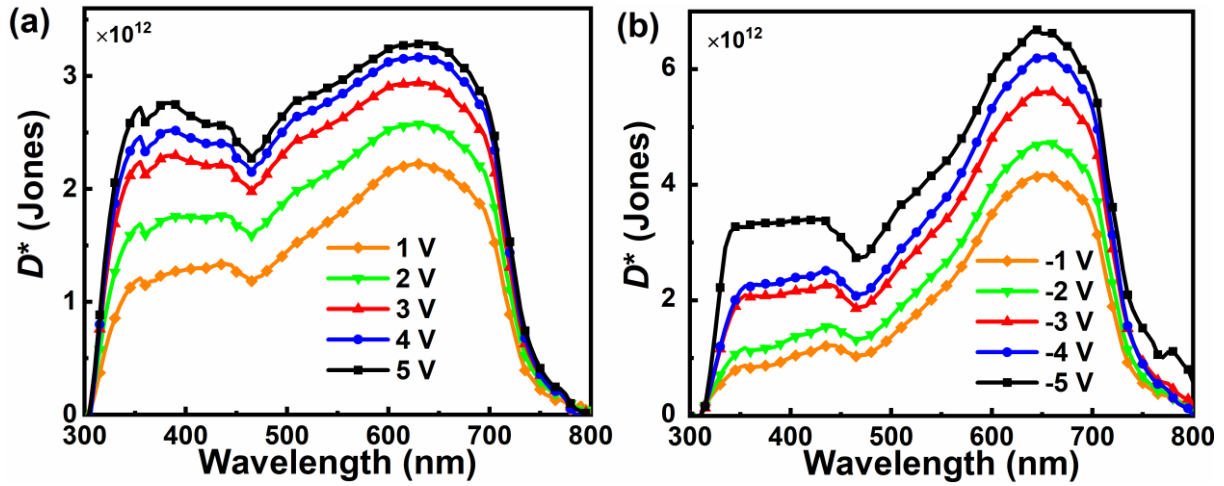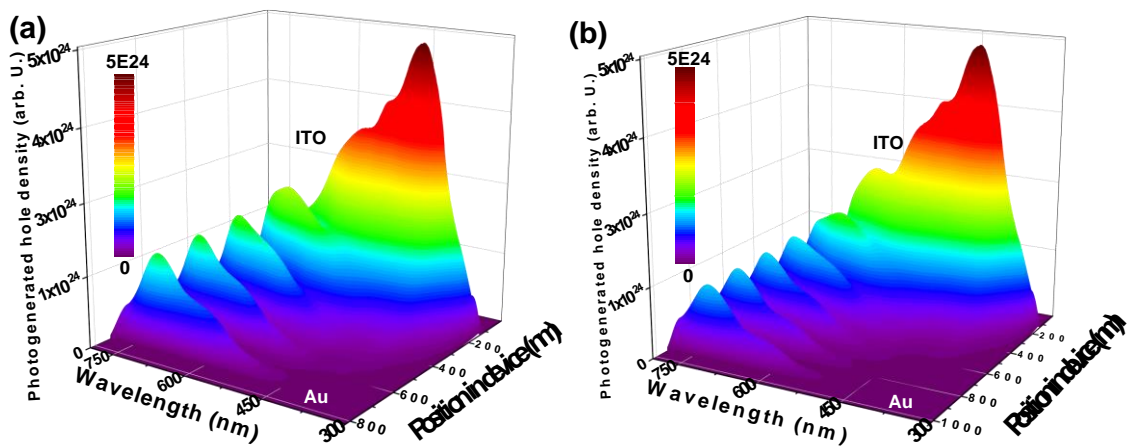
bias.

Figure S7. The specific detectivity (*D**) spectra of the PM type OPDs under different forward and reverse bias.

The *D** values of the PM type OPDs can be markedly improved along with the bias increase, which should be mainly attributed to the enhanced J_{LS} by interfacial trap-assisted electron tunneling injection.
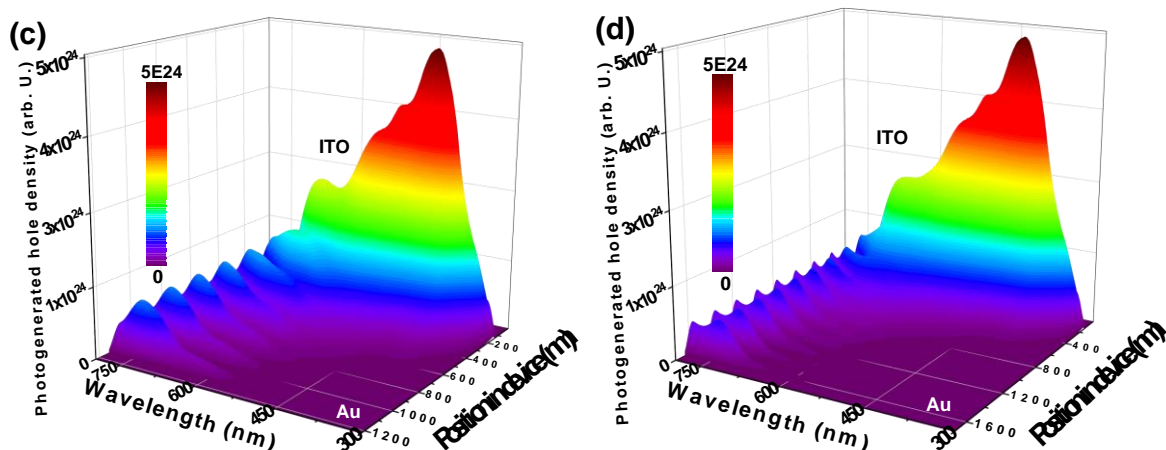
Figure S8. Photogenerated hole distribution in PM type OPDs with different thickness active layers. (a) 600 nm, (b) 800 nm, (c) 1000 nm, (d) 1500 nm.
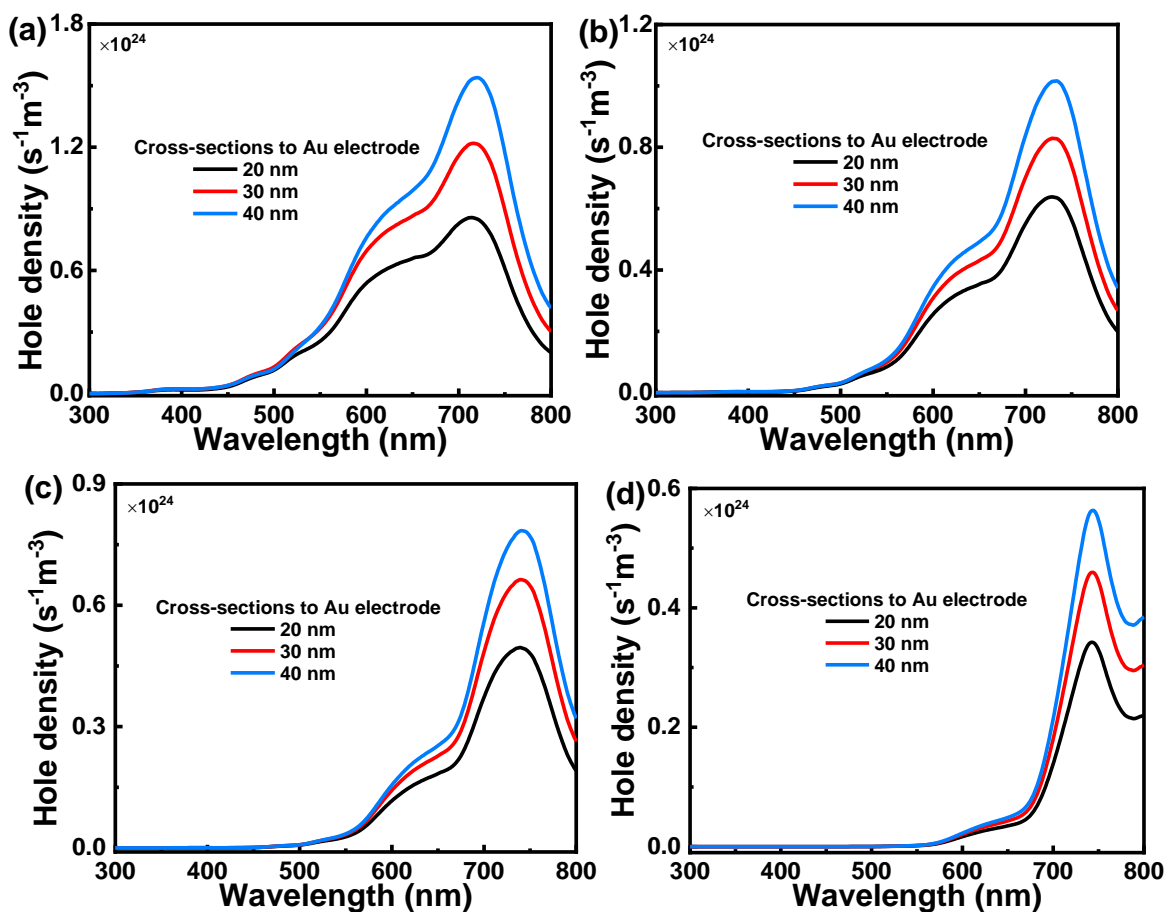

Figure S9. Photogenerated hole density of the PM type OPDs with different active layer thickness on different cross-sections near Au electrode. (a) 600 nm, (b) 800 nm, (c) 1000 nm, (d) 1500 nm.

The photogenerated hole distribution near Au electrode will be narrowed along with the

increase of active layer thickness, which well explains the narrowed spectral response of PM type OPDs with the active layer thickness increasing according to the charge injection narrowing (CIN) concept.

References

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