## **Supporting Information**

# **High Performance Ternary Organic Solar Cells Assisted by Red Fluorescent Materials Through Improved Emission Lifetime and Complementary Short Wavelength Light Absorption**

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#### **4. Experimental details**

#### **4.1 Materials**

PM6 and Y6 were purchased from Solarmer Materials Inc; DCJTB was purchased from Luminescence Technology Corp; Chloroform (CF) was purchased from Sigma-Aldrich Co.  $MoO<sub>3</sub>$  and Ag were purchased from Alfa Aesar Co. The photoactive solution with the blend of PM6, Y6 and DCJTB (the ratio of the PM6:Y6 is 1:1.3, PM6 content is 10 mg  $mL^{-1}$ , DCJTB content were varied according to measurement) was dissolved in CF and stirred overnight. The photoactive solution with the solvent additive of 1-chloronaphthalene (CN)  $(0.5\%, v/v)$ . The ZnO solution was synthesized by a sol-gel method  $1, 2$ .

#### **4.2 Device preparation and characteristics**

Indium–tin-oxide (ITO) glasses were ultrasonicated at 30 °C in isopropyl alcohol, acetone and deionized water for 30 min. The ITO glasses were then dried by a stream of nitrogen and heated on the hot-stage. Firstly, spin-coating ZnO solution on the top of ITO glass (the speed is 3000 rpm and continue 1 min) and baked at 150 °C for 20 min in air (the thickness of ZnO thin films is 20 nm). The photoactive layer solution was spin-coated on the ZnO layer in a  $N_2$ -filled glove box to form the photoactive layer (the speed is 1800 rpm and continue 1 min), and the thermal annealing treatment (120 °C for 15 min, the nominal thickness of  $\sim$ 100 nm). The electron extraction layer of the MoO<sup>3</sup> layer and electrode of Ag films were evaporated under vacuum through a shadow mask to define the active area of the devices  $(2\times2 \text{ mm}^2)$ . The OSC devices have an inverted configuration: ITO/ZnO/D18-Cl:Y6:DCJTB/MoO<sub>3</sub>/Ag. All average

values with standard deviations were calculated from ten parallel devices. The current density versus voltage (*J*–*V*) characteristics of the OSCs were measured in a glove box with a computer-controlled Keithley 236 Source Measure Unit under illumination at 100 mW cm-2 using an AM1.5 G solar simulator. The external quantum efficiency (*EQE*) spectrum was measured with a Stanford Research Systems model SR830 DSP lock-in amplifier coupled to a WDG3 monochromator and a 500 W xenon lamp.

The space-charge-limited-current (SCLC) method was employed to investigate the charge carrier mobility. The charge carrier mobility was measured by the space charge limited current (SCLC) method, and the hole-only and electron-only devices had ITO/PEDOT:PSS/photoactive layer/Au and Al/photoactive layer/Al structures, respectively. The charge carrier mobilities were calculated using the following equation  $3, 4$ :

$$
J=\frac{9}{8}\varepsilon_{r}\varepsilon_{0}\mu\frac{V^{2}}{d^{\beta}}
$$

where *J* is the current density,  $\mu$  is the charge carrier mobility,  $\varepsilon_0$  (8.85×10<sup>-14</sup>) F/cm) and  $\varepsilon$ , are the permittivity of free space and relative permittivity of the material ( $\varepsilon$ <sub>r</sub> was assumed to be 3), respectively, and *V* is the SCLC effective voltage. The charge carrier mobility was calculated using the following equation  $5$ :

$$
\mu = \mu_0 \exp[0.89\gamma \sqrt{\frac{V}{L}}]
$$

where  $\mu_0$  is the charge mobility under zero electric field and  $\gamma$  is a constant. The Mott-Gurney equation can then be described by  $6$ :

$$
J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \frac{V^2}{L^3} \exp[0.89\gamma \sqrt{\frac{V}{L}}]
$$

In this case, the charge mobility were estimated using the following equation  $6$ :

$$
\ln(\frac{J L^3}{V^2}) = 0.89\gamma \sqrt{\frac{V}{L}} + \ln(\frac{9}{8}\varepsilon_r \varepsilon_0 \mu_0)
$$

#### **4.3 XRD Measurement**

The angles at which the peak intensities occur are related to the inter-planar distances of the atomic structure of the photoactive layer and the crystallinity of the photoactive layer; these angles are related by Bragg's law<sup>7</sup>:

### $\lambda = 2d \sin \theta$

where  $\lambda$  is the wavelength of the X-ray radiation used (0.154 nm),  $\theta$  is the peak position half-angle, and *d* is the inter-planar distance.



**Figure S1.** *J-V* characteristics of typical OSCs of PM6:Y6 based binary OSCs, optimized ternary OSCs and high DCJTB ternary OSCs under various light intensities ranging from 100 mW cm<sup>-2</sup> to 5 mW cm<sup>-2</sup> corresponding to Figure S1(a), S1(b) and S1(c), respectively.



**Figure S2.** The XRD curve of neat films (PM6, Y6 and DCJTB) for (a) and three typical films (PM6:Y6 binary film, optimized ternary film and high DCJTB ternary film) for (b).



**Figure S3.** The TEM image of neat PM6, Y6 and DCJTB films.



**Figure S4.** The TEM image of three typical films.



**Figure S5.** The AFM image of neat PM6, Y6 and DCJTB films.



**Figure S6.** The AFM image of three typical films.

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