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# Tuning $V_{oc}$ for High Performing Organic Ternary Solar Cells with Non-fullerene Acceptor Alloys

Yusheng Chen, Pan Ye, Xiangli Jia, Wenxing Gu, Xiaoxi Wu, Xiaozhou Xu, Jianfei Wu, Feng Liu, Zhen-Gang Zhu\*, Hui Huang\*

Y. Chen, P. Ye, X. Jia, X. Wu, J. Wu, Prof. H. Huang

College of Materials Science and Opto-Electronic Technology&Key Laboratory of Vacuum Physic, University of Chinese Academy of Sciences, Beijing 100049, P. R. China

E-mail: huihuang@ucas.ac.cn

W. Gu, Prof. Z. G. ZhuSchool of Electronic, Electrical and Communication Engineering, University ofChinese Academy of Sciences, Beijing 100049, P. R. China

X. Xu

College of Chemistry, Ministry of Education, Beijing Normal University, Beijing 100875, P. R. China

Dr. F. Liu

Department of Physics and Astronomy, Shanghai Jiaotong University, Shanghai, 200240, P. R. China

#### I. Experimental section

#### Materials

PTB7-Th, ITIC-Th and PBDB-T were purchased from Solarmar. TPE-4PDI was synthesized according to the reproted methods.<sup>1, 2</sup>

Synthesis of of FT-2PDI: Under argon atmosphere, 5-bromo-2,9-di(tridecan-7yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H, 9H)-tetraone (1 g, 1.2  $(246 \text{ mg}, 0.6 \text{ mmol})^4$ , and tetrakis(triphenylphosphine)palladium(0) (138 mg, 0.12 mmol) were dissolved in 50 mL toluene. The mixture was heated to reflux overnight, and then cooled to room temperature. A solution of FeCl<sub>3</sub> (1.62 g, 60 mmol) in 10 mL CH<sub>3</sub>NO<sub>2</sub> was added. Then the reactant solution was heated to reflux for 12 h. After the solution cooled to room temperature, the mixture was extracted by chloroform, washed by water and brine, dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub> and the solvent removed under vacuum rot-vap. The crude product was purified by flash chromatography on silica gel to afford FT-2PDI (517.8 mg, yeild: 65.3%) as an orange solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 10.57 (br, 2H), 9.83 (br, 2H), 9.35 (m, 4H), 9.06 (m, 4H), 5.34 (s, 4H), 2.37 (m, 8H), 1.94 (m, 8H), 1.52-1.16 (m, 64H), 0.87 (m, 24H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 164.78, 163.91, 140.57, 133.16, 132.82, 132.00, 131.16, 129.96, 128.83, 127.43, 126.98, 126.59, 125.40, 124.24, 123.67, 123.47, 123.18, 122.34, 55.29, 32.82, 32.48, 32.29, 31.89, 30.46, 29.81, 29.43, 27.26, 23.27, 23.03, 22.77, 22.60, 14.34, 14.23, 14.07. MS (MALDI-TOF, m/z) 1585.3. Anal. Calcd. for C<sub>104</sub>H<sub>120</sub>N<sub>4</sub>O<sub>8</sub>S: C, 78.75; H, 7.63; N, 3.53; Found: C, 77.76; H, 7.58; N, 3.49.

LUMO of ITIC-Th, TPE-4PDI and FT-2PDI were calculated by the electrochemical cyclic voltammetry measurements, bandgap of them were calculated by optical bandgap through bandgap = 1240 /  $\lambda_{offset}$  and HOMO of them were calculated through HOMO = LUMO – bandgap.

#### **Device Fabrication**

Sandwich-structure inverted solar cells consisted of a stack of ITO-coated glass/ZnO/active layer/MoO<sub>3</sub>/Ag. ITO-coated glass substrates were first cleaned by ultrasonic agitation in detergent, deionized water, acetone, and isopropanol in sequence, followed by drying at 80 °C in an oven overnight and then UV ozone treatment for 30 min. 25  $\mu$ L of ZnO precursor (zinc acetate dihydrate) solution was spin-coated on top of the pre-cleaned ITO (4500 rpm, 40 s). After coating, ZnO films were heated at 200 °C for 30 min.

All of the prepared solutions of active layer were chlorobenzene solution, containing 10mg/mL PTB7-Th, 13 mg/mL acceptor and 3% 1-chloronaphthalene as additive or containing 10mg/mL PBDB-T, 10 mg/mL acceptor and 1% 1,8-diiodooctane as additive. The solution was then spin-coated on the substrate to get an active layer. Then, the thin films were transferred into a vacuum evaporator connected to the glove box.  $MoO_3$  (10 nm) and Ag (100 nm) were deposited sequentially by thermal evaporation at a pressure under 10<sup>-5</sup> Pa.

#### **Device Characterization**

The current density-voltage (J-V) characterizations were scanned at 10 mV intervals under air mass (AM) 1.5G using a Newport solar simulator. The average result was got from 15 devices. The input photon to converted current efficiency (IPCE) was measured by Newport IPCE system.

#### **General Measurements**

The electrochemical cyclic voltammetry (CV) measurements were carried out in a solution of tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 M) in acetonitrile as the supporting electrolyte, with a potential scan speed at 0.1 V/s. A glassy-carbon disc, an Ag/AgCl electrode and Pt wire were used as the working electrode, reference electrode and counter electrode, respectively. The film samples of UV-Vis were spin casted on quartz substrates using identical blend solutions as those used in devices. UV-Vis absorption spectra were carried out using a Gary 60 UV-Vis Spectrophotometer. The nanoscale morphology of blend films was observed by NTEGRA Prima in the tapping mode. All film samples of AFM were spin casted on Si substrates. GIXD characterization was performed at beamline 7.3.3 at Lawrence Berkeley National Lab and samples were prepared on Si substrates. Resonant soft X-ray scattering (R-SoXS) measurements were performed at beamline 11.0.1.2 at Lawrence Berkeley National Lab and samples were prepared on Si/PEDOT:PSS substrates.

The geometries of all small molecules were fully optimized by DFT calculation at the B3LYP/(U)B3LYP/6-31G(d,p) level. All the side chain of small molecule were substituted for methyl.

#### **I**. Derivation of energy levels of alloys based on DOS

In our study, we assume that the acceptor 1 (A1) and the acceptor 2 (A2) form the acceptor alloy. The following calculation is explicitly for this case. And the calculation about donor alloys is similar. Here,  $n_1/n_2$  is the molecular number of A1/A2 of unit mass,  $l_1/l_2$  is the number of quasi-degenerate LUMO of per molecule of A1/A2,  $m_1/m_2$  is the weight of A1/A2,  $E_{L1}/E_{L2}$  is the LUMO of A1/A2,  $E_{Le}$  is the effective LUMO of acceptor alloy,  $E_{HOMO}$  is the HOMO of donor.

According to the density of state (DOS) model,  $g_{A1}/g_{A2}$  is the density of state of A1/A2,  $G_{A1}/G_{A2}$  is the density of state of per unit weight of A1/A2,  $g_{eff}$  is the density of state of effective LUMO of alloy,  $G_{eff}$  is the total state of per unit mass of alloy. We use  $V_{oc Ternary}$  to represent the  $V_{oc}$  of the ternary solar cell. And  $V_{oc Binary1}$  and  $V_{oc}$  Binary2 are the  $V_{oc}$  of binary solar cells, i.e. donor:acceptor1 and donor:acceptor2, respectively.

Then, we have the following equations:

$$\begin{split} g_{A1} &= \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2} \right) \,, \\ g_{A2} &= \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \,, \end{split}$$

$$G_{A1} = \frac{n_1 l_1}{\sigma_1 \sqrt{2\pi}} exp\left(-\frac{(E - E_{L1})^2}{2\sigma_1^2}\right),$$
$$G_{A2} = \frac{n_2 l_2}{\sigma_2 \sqrt{2\pi}} exp\left(-\frac{(E - E_{L2})^2}{2\sigma_2^2}\right).$$

Since the acceptors are simply blended without any chemical reaction,  $E_{L1}$  and  $E_{L2}$  do not affect each other. So, the effective density of state can be given by

$$G_{eff} = \frac{\frac{m_1 n_1 l_1}{\sigma_1 \sqrt{2\pi}} exp\left(-\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2}\right) + \frac{m_2 n_2 l_2}{\sigma_2 \sqrt{2\pi}} exp\left(-\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2}\right)}{m_1 + m_2}$$

Introducing ratios  $f_1=m_1/(m_1+m_2)$  and  $f_2=m_2/(m_1+m_2)$ , which can be varied in the fabrication of different ternary solar cells, the G<sub>eff</sub> can be re-expressed as

$$G_{eff} = \frac{f_1 n_1 l_1}{\sigma_1 \sqrt{2\pi}} exp\left(-\frac{(E - E_{L1})^2}{2\sigma_1^2}\right) + \frac{f_2 n_2 l_2}{\sigma_2 \sqrt{2\pi}} exp\left(-\frac{(E - E_{L2})^2}{2\sigma_2^2}\right)$$

We set  $N_{e1}=n_1l_1$  and  $N_{e2}=n_2l_2$ , which means that total electron DOS of unit mass. Thus we get

$$\begin{split} G_{eff} &= f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2} \right) + f_2 \cdot N_{e2} \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ g_{eff} \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2} \right) + f_2 \cdot N_{e2} \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2} \right) + f_2 \cdot N_{e2} \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2} \right) + f_2 \cdot N_{e2} \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2} \right) + f_2 \cdot N_{e2} \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2} \right) + f_2 \cdot N_{e2} \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2} \right) + f_2 \cdot N_{e2} \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2} \right) + f_2 \cdot N_{e2} \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2} \right) + f_2 \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_1^2} \right) + f_2 \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_2^2} \right) + f_2 \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L1}\right)^2}{2\sigma_2^2} \right) + f_2 \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) + f_2 \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma_2^2} \right) \\ &= \frac{f_1 \cdot \frac{1}{\sigma_2 \sqrt{2\pi}} exp \left( -\frac{\left(E - E_{L2}\right)^2}{2\sigma$$

As  $g_{A1}$  and  $g_{A2}$  are the Gaussian distributions, the averaged energy level and disorder of  $g_{eff}$  can be derived in terms of the standard formulas:

$$E_{Le} = \int_{-\infty}^{\infty} Eg_{eff} dE$$
,  
,  
and  $\sigma_{eff}^2 = \int_{-\infty}^{+\infty} (E - E_{Le})^2 g_{eff} dE$ .

After some algebra, we obtain

$$E_{Le} = \frac{f_1 \cdot N_{e1} \cdot E_{L1} + f_2 \cdot N_{e2} \cdot E_{L2}}{f_1 \cdot N_{e1} + f_2 \cdot N_{e2}},$$

(1)

and 
$$\sigma_{eff}^{2} = \frac{f_1 N_{e1} \sigma_1^{2} + f_2 N_{e2} \sigma_1^{2}}{f_1 \cdot N_{e1} + f_2 \cdot N_{e2}} + \frac{f_1 N_{e1} \times f_2 N_{e2}}{(f_1 \cdot N_{e1} + f_2 \cdot N_{e2})^2} \times (E_{L1} - E_{L2})^2$$
(2)

From Eq. (2), it is seen that the effective  $\sigma_{eff}^2$  not only depends on an average of  $\sigma_1^2$  and  $\sigma_2^2$  (the first term of Eq. (2)), but also depends on the energy difference of LUMO 1 and LUMO2, i.e.  $E_{L1}$ - $E_{L2}$ . This energy difference should be regarded as a parameter determined by experiments. Although the DFT calculation can give us a preliminary value for this difference, it is hard to expect a perfect match between the DFT result and the experimental value in a very precise level (the energy resolution in our work

can be 0.01 eV). For convinience, we set 
$$\frac{f_1 N_{e1} \times f_2 N_{e2}}{(f_1 \cdot N_{e1} + f_2 \cdot N_{e2})^2} \times (E_{L1} - E_{L2})^2 = M$$

In organic solar cell, we assume that direct bimolecular recombination is the dominant form of recombination. In this case, the recombination rate can be expressed as:

$$G = \gamma n_h(x) n_e(x)$$

where  $n_{\rm h}$  (x) and  $n_{\rm e}$  (x) are the carrier density of hole and electron and  $\gamma$  is the recombination rate coefficient.

The carrier densities of hole and electron are calculated by integrating the Fermi-Dirac distribution across the density of state. A low carrier densities, the result can be approximated by a Boltzmann distribution.  $N_{\rm h}$  and  $N_{\rm e}$  are total state for hole and electron. For acceptor alloy,  $N_{\rm e} = f_1 N_{\rm e1} + f_2 N_{\rm e2}$ .

$$n_h(x) = N_h \exp\left(\frac{\sigma_D^2}{2(k_B T)^2}\right) \exp\left(\frac{E_{HOMO, D} - E_{F, h}}{k_B T}\right)$$

$$n_e(x) = N_e \exp\left(\frac{\sigma_A^2}{2(k_B T)^2}\right) \exp\left(\frac{E_{F,e} - E_{LUMO,A}}{k_B T}\right)$$

Combined these three equation, we can get an expression for the  $V_{oc}$  of solar cell.

$$eV_{OC} = E_{LUMO,A} - E_{HOMO,D} - \frac{\sigma_D^2}{2k_BT} - \frac{\sigma_A^2}{2k_BT} + k_BTLn\left(\frac{G}{\gamma N_h N_e}\right)$$

For acceptor ternary solar cell, the energy level of donor was considered unchanged, and LOMO and energy disorder of acceptor alloy was considered as the result of mixing of all acceptors orbitals. And it is assumed that the recombination rate and the recombination rate coefficient is unchanged when the mixing of acceptor is varying. So, replaced the  $E_{\text{LUMO},\text{A}}$  and  $\sigma_{\text{A}}$  by  $E_{\text{Le}}$  and  $\sigma_{\text{eff}}$ , the equation about the  $V_{\text{oc}}$  of ternary solar cell can be expressed as:

$$eV_{OCTernary} = \frac{f_1 N_{e1} E_{LOMO,A1} + f_2 N_{e2} E_{LOMO,A2}}{f_1 N_{e1} + f_2 N_{e2}} - E_{HOMO,D} - \frac{\sigma_D^2}{2k_B T} - \frac{\sigma_{eff}^2}{2k_B T} + k_B T Ln \left(\frac{G}{\gamma N_h}\right) + k_B$$
$$T Ln \left(\frac{1}{f_1 N_{e1} + f_2 N_{e2}}\right)$$

When  $f_1 = 1$ ,  $f_2 = 0$ , or  $f_1 = 0$ ,  $f_2 = 1$ ,  $V_{oc}$  of binary solar cells can be calculated as below

$$eV_{OC Binary1} = E_{LOMO, A1} - E_{HOMO, D} - \frac{\sigma_D^2}{2k_BT} - \frac{\sigma_1^2}{2k_BT} + k_BTLn\left(\frac{G}{\gamma N_h}\right) + k_BTLn\left(\frac{1}{N_{e1}}\right),$$
$$eV_{OC Binary2} = E_{LOMO, A2} - E_{HOMO, D} - \frac{\sigma_D^2}{2k_BT} - \frac{\sigma_2^2}{2k_BT} + k_BTLn\left(\frac{G}{\gamma N_h}\right) + k_BTLn\left(\frac{1}{N_{e2}}\right).$$

So, as a result, we can get the equation

$$eV_{OCTernary} = \frac{f_1 N_{e1} V_{ocBinary1} + f_2 N_{e2} V_{OCBinary2}}{f_1 N_{e1} + f_2 N_{e2}} - \frac{M}{2k_B T} - k_B T \times \left[ Ln \left( \frac{1}{f_1 N_{e1} + f_2 N_{e2}} \right) + \frac{1}{2k_B T} \right]$$

When the value of  $N_e$  is about 10<sup>20</sup>, the third term of the right side of this equation varies typically in the range of 0 to 0.001, which indicated it can be ignored. And we

find that the first part of this equation can fit the experiment date well, which indicated the value of M is experimentally tested to be very small and can be ignored too. So, the equation can be re-expressed as:

$$eV_{OCTernary} = \frac{f_1 N_{e1} V_{oc Binanry1} + f_2 N_{e2} V_{OC Binary2}}{f_1 N_{e1} + f_2 N_{e2}}$$

The conclusion is same as the result we have published.<sup>5</sup>

## **II**. Figures



Fig. S1 (a, b, c) The pictorial representations of the frontier molecular orbitals of ITIC-Th, TPE-4PDI and FT-2PDI from the DFT calculations, respectively.



Fig. S2 Cyclic voltammetry measurements of the acceptor alloys of ITIC-Th and TPE-4PDI in different weight ratios.



Fig. S3 Cyclic voltammetry measurements of the acceptor alloys of ITIC-Th and FT-2PDI in different weight ratios.



Fig. S4 Chemical structures of DR3TSBDT, DRCN5T, SF-4PDI, TPE-4PDI(OD), and PCBM(70).



Fig. S5 (a, b, c) The pictorial representations of the frontier molecular orbitals of SF-4PDI, DRCN5T and DR3TSBDT from the DFT calculations, respectively.



Fig. S6 (a, b, c, d, e) The 1  $\mu$ m×1  $\mu$ m height images of AFM for ternary blend films with 0%, 10%, 25%, 50% and 100% TPE-4PDI respectively.



Fig. S7 (a, b, c, d, e) The 1  $\mu$ m×1  $\mu$ m phase images of AFM for ternary blend films with 0%, 10%, 25%, 50% and 100% TPE-4PDI respectively.



Fig. S8 The in-plane and out-of-plane cuts of GIXD measurements.



Fig. S9 (a, b, c, d, e) RSoXS profiles with a series of photon energies close to the carbon K edge of ternary blend films with TPE-4PDI ratio of 0%, 3%, 10%, 25%, and 100%.



Fig. S10 (a, b, c, d, e) TEM images of ternary blend films with TPE-4PDI ratio of 0%, 3%, 10%, 25%, and 100%.



Fig. S11 (a, b) The J-V curve and EQE curve of PBDB-T based ternary solar cell.



Fig. S12 <sup>1</sup>H NMR spectra of FT-2PDI.

### **IV**. Tables

Table S1. Device data of OSCs based on PTB7-Th:ITIC-Th:TPE-4PDI in different weight ratios.

PTB7-Th:ITIC-Th:TPE-4PDI	PCE(%)	$V_{\rm oc}({ m V})$	$J_{\rm sc}/{ m mA}{\cdot}{ m cm}^{-2}$	FF(%)
77:100:0	8.25±0.09	0.78±0.01	15.78±0.06	67.5±0.5
77:90:10	9.07±0.11	0.80±0.01	16.62±0.10	68.2±0.5
77:75:25	7.69±0.13	0.82±0.01	15.60±0.12	60.7±0.6
77:50:50	5.97±0.09	0.84±0.01	13.58±0.13	52.7±0.4
77:0:100	4.90±0.08	0.88±0.01	11.78±0.04	48.1±0.7

Table S2. Device data of OSCs based on PTB7-Th:ITIC-Th:FT-2PDI in different weight ratios.

PTB7-Th:ITIC-Th:FT-2PDI	PCE(%)	$V_{\rm oc}({ m V})$	$J_{\rm sc}/{ m mA}\cdot{ m cm}^{-2}$	FF(%)
77:100:0	8.25±0.09	0.78±0.01	15.78±0.06	67.5±0.5
77:90:10	8.57±0.09	0.79±0.01	16.04±0.15	67.8±0.5
77:75:25	8.87±0.13	0.81±0.01	16.10±0.12	68.0±0.4
77:50:50	7.45±0.15	0.83±0.01	15.99±0.23	56.1±0.3
77:0:100	2.64±0.16	0.88±0.01	6.64±0.42	44.9±0.4

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