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# Ternary Organic Solar Cells: Using Molecular Donor or Acceptor Third Components to Increase Open Circuit Voltage

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## **Supporting Information**

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## 1. Materials and Methods

**Materials:** All reactants, reagents, and catalysts were purchased from Sigma-Aldrich. All solvents and materials purchased were used without further purification. PBDB-T polymer was purchased form Brilliant Matters [1].

**UV-Visible Spectroscopy (UV-Vis):** All optical absorption measurements were recorded using Agilent Technologies Cary 60 UV-Vis spectrometer at room temperature. All solution UV-Vis experiments were run in CHCl<sub>3</sub> using 10 mm quartz cuvettes. Films were spin-cast into Corning glass micro slides. Prior to use, glass slides were cleaned with soap and water, acetone and isopropanol, and followed by UV/ozone treatment using a Novascan UV/ozone cleaning system.

**Atomic Force Microscopy (AFM):** AFM measurements were performed by using a TT2- AFM (AFM Workshop) in tapping mode and WSxM software with a resonance frequency of 300 kHz, a force constant of 40 N/m and a reflective back side aluminum coating (Tap300Al-G, BudgetSensors). Samples for AFM measurements were the same ones that were used to collect the respective device parameters.

**Solar Cells Fabrication and Testing:** Solar cells were fabricated on ITO-coated glass substrates, which were first cleaned by sequentially ultra-sonicating detergent and de-ionized water, acetone and isopropanol before use. ITO substrates were first pretreated under UV-ozone for 30 minutes. ZnO was deposited as a sol-gel precursor solution in air following the method of Sun et al. [2]. The room temperature solution was filtered and spin-cast at a speed of 4000 rpm and then annealed at 200 °C in air for fifteen minutes.

Active materials: PBDB-T (**D1**), PC[60]BM (A1)

Active additives: tBTI-IDT (**D2**), tPDI<sub>2</sub>N-Hex (**A2**)

Active layer solutions were prepared in chlorobenzene (CB) with 3% wt. 1,8-diiodooctane (DIO) additive. The total concentration of mixed **PBDB-T:PC[60]BM (D1:A1)** was 10 mg ml<sup>-1</sup> for all solvents. The substrates were then kept in an N2 atmosphere glovebox overnight before evaporating MoO<sub>3</sub> and Ag. The evaporation of 10 nm of MoO3 followed by 100 nm of Ag were thermally deposited under vacuum ( $2x10^{-6}$  Torr).

Current density-voltage (J-V) characteristics were measured using a Keithley 2420 Source Measure Unit. Solar cell performance used an Air Mass 1.5 Global (AM 1.5G) Solar Simulator (Newport, Model 92251A-1000) with an irradiation intensity of 100 mW cm<sup>-2</sup>, which was measured by a calibrated silicon solar cell and a readout meter (Newport, Model 91150V).



## 2. Optical Absorption Spectra and Device Characteristics of OSCs

Figure S1) Absorption spectra and J-V curves of the PBDB-T:PC[60]BM (1:1, D1:A1) solar cells processed with and without DIO solvent additive.



Figure S2) Absorption spectra and J-V curves of the PBDB-T:PC[60]BM (1:1. D1:A1) inverted and conventional OSCs.



**Figure S3)** Normalized absorption spectra and J-V curves of the D1:D2:A1 OSCs with varying weight ratios of active materials used in the processing solutions.



**Figure S4)** Normalized absorption spectra and J-V curves of the D1:A1:D2 OSCs with varying weigh ratios of active materials used in the processing solutions.



**Figure S5)**  $J_{dark}$  (left) and  $J_{total}$  (right) of D1:A1, D1:D2:A1 and D1:A1:A2 OSCs with a standard D1:D1 weight ratio of 1:1 with 0.2 of D2 or A2 added in the processing solutions.



Figure S6) Absorption spectra and J-V curves of PBDB-T:tPDI-Hex solar cells at different concentration DIO.

Active Layer	additive*, %	Ratio	$V_{OC}, \mathbf{V}$	$J_{SC}$ , mA cm <sup>-2</sup>	FF, %	PCE, %	
D1:A1	-	1:1	0.90	14.98	58.3	7.90	
D1:A1	3	1:1	0.80	14.53	69.1	8.07	
D2:A1**	-	1:3	1.03	6.74	28.0	1.94	
D1:D2:A1	3	1:0.2:1	0.86	13.53	71.8	8.40	
D1:D2:A1	3	1:0.5:1	0.92	12.32	65.3	7.42	
D1:D2:A1	3	1:0.8:1	0.95	10.65	61.4	6.23	
D1:A1:A2	3	1:0.2:1	0.87	15.97	60.5	8.25	
D1:A1:A2	3	1:0.5:1	0.91	15.02	58.4	8.03	
D1:A1:A2	3	1:0.8:1	0.94	14.28	57.1	7.68	
D1:A2	-	1:1	1.06	7.31	45.3	3.51	
D1:A2	0.5	1:1	1.04	6.26	50.7	3.29	
D1:A2	1	1:1	1.03	7.52	48.8	3.79	
*1,8-diiodooctane (DIO) additive in chlorobenzene solvent							
** - data from the paper [3]							

Table S1) Tabulated	data for both bi	nary and terna	ary solar cells.

# 3. AFM-images of OSCs



**Figure S7)** Atomic force microscopy height images of ternary system D1:D2:A1 with 1:0.5:1 ratio (RMS=1.642) (left) and (b) with 1:0.8:1 ratio (RMS = 2.388 nm) (right).



**Figure S8)** Atomic force microscopy height images of ternary system D1:A1:A2 with 1:1:0.5 ratio (RMS=2.852) (left) and (b) with 1:1:0.8 ratio (RMS = 4.630nm) (right).

#### 4. Organic Field Effect Transistors

**OFET Fabrication**: Bottom-gate, bottom-contact organic thin-film transistors were made using prefabricated Si/SiO<sub>2</sub> substrates with gold source-drain contacts (L = 30  $\mu$ m, W=1 mm). The substrates were rinsed with detergent and de-ionized water, acetone and isopropanol before being dried with nitrogen and placed in scintillation vials with 1% v/v octyltrichlorosilane (OTS, 97%) in anhydrous toluene. Sealed vials were heated at 70 °C for 1 hour then removed, rinsed with toluene, then dried with nitrogen and heated at 70 °C for 1 hour in vacuum to remove residual solvent. Drop cast devices were made by placing 1  $\mu$ L droplets of 10 mg/mL solutions of **PBDB-T:PC[60]BM, PBDB T:tBTI-IDT:PC[60]BM or PBDB-T:PC[60]BM:tPDI-Hex** in C<sub>6</sub>H<sub>5</sub>Cl with 3% C<sub>12</sub>H<sub>10</sub>O (10 mg/mL) onto the channels and leaving them to dry. These devices were dried at 70 °C for an hour to evaporate residual solvent.

**OFET Testing**: Prepare OFETs were transferred into an plastic glovebox with nitrogen atmosphere. Output and transfer characteristics were obtained for each device with  $L = 30 \mu m$ . For transfer curves, data was collected at  $V_{DS} = -80$  and 80V. The electron and hole saturation field-effect mobility ( $\mu_e$  and  $\mu_h$ ) were calculated using following equation:

$$I_{DS} = \frac{W}{2L} \mu C (V_{GS} - V_T) \tag{2}$$

where L and W are the length and width of the conductive channel, respectively,  $\mu$  the carrier mobility and C the capacitance per unit area (in F/cm<sup>2</sup>),  $V_{GS}$  is the bias between the gate and source,  $I_{DS}$  is the current between the source and drain,  $V_T$  (threshold voltage) is the voltage at which the formation of an inversion layer between the isolating layer and the substrate allows for a non-negligible drain-source current.

	$\mu_h$ , (max)	$\mu_h$ , (avr)	$\mu_{e}$ , (max)	$\mu_{e}$ , (avr)	$\mu_h/\mu_e$
	$(cm^2 V^{-1} s^{-1})$	$(cm^2 V^{-1} s^{-1})$	$(cm^2 V^{-1} s^{-1})$	$(cm^2 V^{-1} s^{-1})$	
PBDB-T (D1)	6.96*10-2	4.67*10 <sup>-2</sup>	-	-	-
PBDB-T:PC[60]BM (D1:A1, 1:1)	6.04*10-2	4.57*10-2	1.43*10-1	7.1*10-2	0.64
PBDB-T:PC[60]BM:tPDI-Hex (D1:A1:A2, 1:1:0.2)	6.07*10-2	4.11*10-2	9.77*10 <sup>-2</sup>	5.7*10-2	0.72
PBDB-T:tBTI-IDT:PC[60]BM (D1:D2:A1, 1:0.2:1)	4.76*10-2	3.11*10-2	1.06*10-1	6.54*10-2	0.48

Table S2. Summary of devices mobilities incorporating different materials.

#### 5. Charge Carrier Dynamics

To understand the high performance of binary and ternary OSCs, we investigated the relationship between photocurrent  $(J_{ph})$  and effective voltage  $(V_{eff})$  to evaluate the charge generation and collection in the OSCs. As shown in Fig. S10a,  $J_{ph}$  is given by  $J_{ph} = J_{total} - J_{dark}$ , where  $J_{total}$  and  $J_{dark}$  represent the photocurrent densities under light illumination and dark condition, respectively.  $V_{eff}$  is defined as  $V_{eff} = V_0 - V_{appl}$ , where  $V_0$  is the voltage when  $J_{ph} = 0$  and  $V_{appl}$  is the applied voltage [4–6]. The  $J_{ph,sat}$  is saturated at a  $V_{eff}$  of ~2 V for binary system, and 1.6 V and 1.2 V for ternary D1:D2:A1 and D1:A1:A2 OSCs, respectively. The charge collection probability  $P_c(I,V)$  is defined as  $J_{ph}/J_{ph,sat}$ . When it is assumed that the internal field is large enough to extract most of photo-generated charges to electrodes at sufficiently large reverse bias which leading to  $P_c(I,V)$  close to 100%. It is calculated that the  $P_c(I,V)$  values under maximal power output condition are 79%, 83% and 79%, respectively, for the OSCs based on the D1:A1 (1:1), D1:D2:A1 (1:0.2:1), and D1:A1:A2 (1:1:0.2) blends. The results show that incorporation of A2 facilitates charge dissociation in the ternary bland system.

To gain deeper insight into the charge recombination kinetics, we studied the variation of  $J_{SC}$  as a function of light intensity (Fig. S10b). The measured curves shown on Fig. S10b were fitted according to the power law equation:  $J_{SC} \propto I^{\alpha}$ , where *I* is the intensity of incident light and  $\alpha$  is an exponent constant, which becomes 1 if all of the dissociated charges are extracted to the electrodes. In all systems, the  $\alpha$  value is less than one. This deviation from  $\alpha = 1$  is typically attributed to the bimolecular recombination, space charge effects, and variations in mobility between the two carriers [4,7].

We studied the charge carrier mobility as determined by organic field-effect transistor (OFET) measurements. The electron and hole mobilities in the BHJ film are  $\sim 4*10^{-2}$  and  $6*10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, and do not change when moving from binary to ternary blends (Table S2). These values are similar and indicate balanced charge carrier mobilities. Therefore, variations in mobility between the two carriers and space charge effects are not responsible for the slight decrease in  $\alpha$  ( $\alpha \sim 0.94$ -0.96, Fig. S10b), and thus bimolecular recombination exists.

When bimolecular (Langevin) recombination is the sole loss mechanism, the  $V_{OC}$  of the OSCs is given by the equation:

$$V_{OC} = \frac{E_{gap}}{q} - \frac{AkT}{q} ln^{[m]} [\frac{(1 - P_c)\gamma N_c^2}{P_c G}]$$
<sup>(2)</sup>

where  $E_{gap}$  is the energy difference between the highest occupied molecular orbital (HOMO) of the donor and lowest unoccupied molecular orbital (LUMO) of the acceptor, q is the elementary charge, k is the Boltzmann constant, T is temperature in Kelvin,  $P_C$  is the dissociation probability of the electron-hole pairs,  $\gamma$  is the Langevin recombination constant,  $N_C$  is the effective density of states, and G is the generation rate of bound electron-hole pairs [4,8–10]. Since G is the only term directly proportional to the light intensity ( $P_C$  and  $\gamma$  are independent of it), the slope of the  $V_{oc}$  versus the natural logarithm of the light intensity gives kT/q for bimolecular recombination. Fig. S10c shows a linear relationship where the slope is greater than 1 kT/q in the presence of trap-assisted (so called Shockley-Read-Hall, SRH) charge recombination. Thus, slight deviation in 1.1-1.2 kT/q in our binary and ternary OSCs indicate the additional mechanism of SRH recombination is involved, which competes with bimolecular recombination.



**Figure S9).** (a)  $J_{ph}$ - $V_{eff}$  curves of optimized binary and ternary OSCs. (b) Measured  $J_{SC}$  of optimized binary and ternary OSCs plotted against light intensity (symbols) on a logarithmic scale. Fitting a power law (dash line, eq.  $J_{SC} \propto I^{\alpha}$ ) to these data yields  $\alpha$ . (c) Measured  $V_{OC}$  of optimized binary and ternary OSCs as a function of illumination intensity (symbols), together with linear fits to the data (dash lines).

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