## **Supporting Information**

## **Constructing a Dual-Fiber Network in High Efficiency Organic Solar Cells via Additive-Induced Supramolecular Interactions with Both Donor and Acceptor**

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### 1. Instrument and test parameters

UV-vis absorption spectra were recorded using a PerkinElmer UV-vis spectrometer, model Lambda 750. Photoluminance (PL) measurements were measured with a PL microscopic spectrometer (Flex One, Zolix, China) with a 660 nm CW laser. FTIR spectra were recorded on a Thermo Scientific Nicolet iS50. The electrochemical properties were characterized by cyclic voltammetry (CV) using a CHI 630A Electrochemical Analyzer with a three-electrode electrochemical cell. The analysis was conducted in a 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> CH<sub>3</sub>CN solution under a nitrogen atmosphere, with a scanning rate of 0.1 V/s. A platinum working electrode, a platinum wire counter electrode, and an Ag/AgNO<sub>3</sub> (0.01 M in CH<sub>3</sub>CN) reference electrode were used. The ferrocene/ferrocenium (Fe/Fe<sup>+</sup>) redox couple was used as the internal reference standard. We applied the formula  $E_{\text{HOMO/LUMO}} = -$  (Eonset Ox - E1/2 Fe/Fe<sup>+</sup> + 4.8) eV to determine the HOMO/LUMO energy levels. GIWAXS data were obtained at the 1W1A Diffuse X-ray Scattering Station at the Beijing Synchrotron Radiation Facility (BSRF-1W1A). Samples were prepared by spin-coating under device conditions on Si substrates. Transmission electron microscopy (TEM) images were obtained using an FEI Technai TF20 (Philips) transmission electron microscope. Atomic force microscopy (AFM) images were acquired using a Nanoscope VIII MultiMode AFM (Bruker) in tapping mode, with silicon tips (TESP) probes having a resonant frequency of ~300 kHz and a spring constant of ~40 N/m. In situ UV-vis absorption measurements were performed using a DU-100 system, with the optical fiber aligned to focus the light on the center of the film. The sampling interval was 1 ms, with an integration time of 80 ms per sample point. We conducted an in-depth study of hole

transfer dynamics by recording the **femtosecond transient absorption (fs-TA)** spectra of blend films. Due to the significant differences in the absorption ranges of PM6 and L8-BO in the blend films, a low-power 800 nm pump beam was used to selectively excite the acceptor. AFM topography images and corresponding chemical IR imaging were acquired using a NanoIR3 (Bruker) at Nanjing Forestry University. We employed contact-mode NanoIR3 probes (model: PREX-nIR3, Bruker) with a resonance frequency of  $13 \pm 4$  kHz and a spring constant of 0.07-0.4 N/m. **The AFM-nano-IR technique** involved coupling a pulsed tunable IR source with an AFM, focusing the light on the tip-sample contact area. Absorption of the pulsed light by the sample caused rapid heating and expansion, generating an impulse on the AFM cantilever and inducing oscillation. The oscillation amplitude of the cantilever was directly proportional to the IR absorption coefficient of the sample.

### 2. Fabrication and characterization of organic solar cells

#### 2.1 The preparation process of OSCs

Pre patterned ITO coated glass substrate were cleaned with detergent and placed in a PTFE cleaning rack for 20 minutes of ultrasonic treatment in deionized water, acetone, and isopropanol, followed by overnight drying in an oven. The photovoltaic capabilities of the donor polymers were assessed by fabricating conventional organic solar cells (OSCs) with a device configuration of ITO/2PACz/PM6:L8-BO (100 nm)/PDINN (8 nm)/Ag (100 nm). 2PACz was spin-cast onto the ITO surface at 5200 rpm for 16 seconds and baked at 70°C for 3 minutes in air. PM6 concentration was 7.5 mg/mL in chloroform, with a donor/acceptor (D/A) ratio of 1:1.2. The concentration of additives is provided in Table S1. The solution was heated to 60°C to ensure complete dissolution of solids, then cooled to 30°C for spin coating. The active layer was spincoated in a nitrogen-filled glove box to a thickness of 100 nm and then annealed on a hot stage. Once fully cooled, a methanol solution of PDINN (1.5 mg/mL) was spincoated onto the BHJ layer at 3000 rpm for 20 s. Finally, a 100 nm Ag layer was thermally deposited under vacuum (below 10<sup>-7</sup> Torr). Photovoltaic cells were fabricated on substrates with an area of  $4 \text{ mm}^2$ . The *J-V* curves were recorded in a glove box at approximately 25°C using an instrument from Enli Technology Ltd., Taiwan (SSF53A) under AM 1.5G illumination (AAA class solar simulator, with an intensity of 100 mW cm<sup>-2</sup> calibrated with a standard single crystal Si photovoltaic cell). External quantum efficiency (EQE) measurements were conducted in air without encapsulation using a solar cell spectral response measurement system (QER3011, Enli Technology Co. Ltd), with intensity calibrated against a standard single crystal Si photovoltaic cell. The stability of all devices was assessed using an ITO/2PACz/PM6: L8-BO (100

nm)/PDINN (8 nm)/Ag (100 nm) structure for placement stability, while an ITO/ZnO/PM6:L8-BO (100 nm)/MoO<sub>3</sub> (8 nm)/Ag (100 nm) structure was utilized for evaluating thermal and photo stability. The ITO-coated glass and PTFE cleaning rack were purchased from Advanced Election Technology CO.,Ltd and methanol, acetone, isopropanol and other reagents were purchased from Energy Chemical.

### 2.2 The computational process of $P_{\rm diss}/P_{\rm coll}$ and $\mu_{\rm h}/\mu_{\rm e}$

Exciton dissociation ( $P_{diss}$ ) and charge collection ( $P_{coll}$ ) efficiencies were calculated from the  $J_{ph}$  versus  $V_{eff}$  curves.  $J_{ph} = J_L - J_D$ , where  $J_L$  and  $J_D$  are the current densities under illuminated and dark conditions, respectively.  $V_{eff}$  is the difference between the applied voltage (V) and  $V_0$ , the compensation voltage at  $J_{ph} = 0$ . The exciton dissociation probability ( $P_{diss}$ ) was calculated as  $J_{ph'}/J_{sat}$ , where  $J_{sat}$  is the saturation photocurrent density. To further investigate the impact of multi-scale fiber morphology on charge transport performance, we employed the Space Charge Limited Current (SCLC) method to measure hole/electron mobility ( $\mu_h/\mu_e$ ) of PM6: L8-BO hybrid devices.<sup>[1]</sup> The structures for these measurements were: ITO/ 2PACz/ Polymer Donor: Acceptor/ MoO<sub>3</sub>/ Ag for hole-only devices and ITO/ ZnO/ Polymer Donor: Acceptor/ PDINN/ Ag for electron-only devices. The formula  $J = 9\varepsilon_r\varepsilon_0\mu/(8L^3)V^2$  was used to calculate the mobilities, where J is the space charge limited current,  $\varepsilon_0$  is the vacuum permittivity ( $\varepsilon_0$  $\approx 8.85 \times 10^{-12}$  F/m),  $\varepsilon_r$  is the relative permittivity of the active layer material,  $\mu$  is the charge mobility at zero field, L is the thickness of the active layer, and V is the applied voltage.

### 2.2 The Calculated process of exciton diffusion length

We utilized the exciton-exciton annihilation (EEA) model and transient absorption spectrum measurement techniques to precisely determine the  $L_D$  of four neat PM6 and L8-BO films.<sup>[2-4]</sup> The formula used to calculate  $L_D$  is  $L_D = (D\tau)^{1/2}$ , where *D* represents the diffusion coefficient and  $\tau$  represents the exciton lifetime.  $L_D$  is corresponding to the exciton lifetime  $\tau$  and the diffusion coefficient *D*. The value of exciton lifetime  $\tau$ was received through multi-exponential fitting method. And the calculation formula is as follows:

$$I(t) = A_1 e^{-t/\tau 1} + A_2 e^{-t/\tau 2} + A_3 e^{-t/\tau 3}$$
$$\tau = A_1 \times \tau_1 + A_2 \times \tau_2 + A_3 \times \tau_3$$

Where  $A_i$  is the proportion of the corresponding lifetime  $\tau_i$ . Exciton quenching is generally associated with bimolecular EEA and trap-induced recombination. According

to the EEA model, there are two main quenching channels for excitons, i.e., trapassisted recombination and bimolecular EEA recombination, corresponding with two decay rate parameters of  $\kappa$  and  $\gamma$ , respectively. The values of *D* can be calculated by  $\kappa$ and  $\gamma$ . The relationship between  $\kappa$  and  $\gamma$  is shown as follows:

$$-\frac{dn(\tau)}{d\tau} = \kappa n(\tau) + \gamma n^{2}(\tau)$$
$$n(\tau) = \frac{n(0)exp^{[m]}(-k\tau)}{1 + \frac{\gamma}{\kappa}n(0)[1 - exp^{[m]}(-\kappa\tau)]}$$

Where,  $n(\tau)$  is the exciton density at a decay time of  $\tau$ . The four neat PM6/L8-BO films are pumped at 630/844 nm with different excitation intensities of 2.63/0.19 and 23.58/3.83 µJ cm<sup>-2</sup>, and the corresponding GSB signals (as shown in Figure S12) are recorded to determine the decay rate parameters of  $\kappa$  and  $\gamma$ . When a low excitation intensity of 2.63/0.19 µJ cm<sup>-2</sup> is applied, the EEA effect disappears and the decay dynamics are approximately monoexponentially, which obeys the equations as follows:

$$\frac{dn(\tau)}{d\tau} = kn(\tau)$$

Thus, the corresponding  $\kappa$  values of the PM6/L8-BO films without/with TZ-Cl, TZ-2Cl and TZ-3Cl are 36.87/20.09, 33.16/19.95, 35.01/15.47 and 36.67/23.45×10<sup>9</sup> s<sup>-1</sup>, respectively. Besides, when a high excitation intensity of 23.58/3.83 µJ cm<sup>-2</sup> is applied, the EEA effect occurs and results in different decay dynamics, thus we can obtain the following equations:

$$\tau_{1/2} = \frac{\alpha \ln 2}{\kappa}, \alpha < 1$$
$$\gamma = \frac{\kappa (2\exp(\alpha \ln 2) - 1)}{n_0 (1 - \exp(-\alpha \ln 2))}$$

Where  $\tau_{1/2}$  is the time of the exciton concentrations decay to 1/2. The corresponding

 $\tau_{1/2}$  values of the blend films PM6 films without/with TZ-Cl, TZ-2Cl and TZ-3Cl are are 14.65/5.85, 14.64/5.50, 13.70/6.10 and 13.65/5.50 ps when a high excitation intensity was used. Therefore, the values of  $\gamma$  are 0.76/11.00, 0.74/11.94, 0.85/11.38

and  $1.05/11.62 \times 10^{-8}$  cm<sup>3</sup> s<sup>-1</sup> respectively. Then the diffusion coefficient *D* can be calculated by the equation as follow:

$$D = \frac{\gamma}{4\pi R}$$

where R is the annihilation radius of singlet excitons. R is assumed to be 2 nm.

### 2.3. The methods of theoretical calculations

All molecules were optimized with Gaussian 09 under B3LYP/6-31G (d, p) level.<sup>[5]</sup> Molecular electrostatic potential (ESP) distributions were calculated through density functional theory (DFT) under B3LYP/6-311G (d, p) with Gaussian 09 and plotted with VMD 1.9.4.<sup>[6]</sup> To quantify intermolecular interactions between additives (**TZ-CI**, **TZ-2CI**, and **TZ-3CI**) and the active layer materials, the binding energies ( $\Delta E_b$ ) between PM6/L8-BO and additives were calculated under B3LYP-D3(BJ)/6-311G (d, p) with Gaussian 09. All configurations to calculate  $\Delta E_b$  were extracted from equilibrated molecular dynamics (MD) simulations. Details for MD simulations were described in next paragraphs.

All MD simulations were performed with GROMACS 2021.3 software.<sup>[7]</sup> The Generalized Amber Force Field (GAFF2) parameters were used to describe the bonded and non-bonded interactions of all studied molecules and the solvent chloroform. For PM6 donor, the degree of polymerization of 4 was used. The LINCS algorithm was used to constrain all bonds.<sup>[8]</sup> For non-bonded interactions, the Particle-Mesh-Ewald (PME) summation method was used to calculate electrostatic interactions with the cutoff at 10 Å. For van der Waals, a 10 Å cutoff was also set.<sup>[9]</sup>

The number of molecules for MD simulations was determined from the experimental feed composition. Initial structures were constructed in the 15×15×15 nm<sup>3</sup> box with embedded program in the GROMACS. For each system, simulation protocol consisted of a 50 ns NPT ensemble equilibrium MD simulation under solvation conditions, a quasi-equilibrium MD approach to model the solvent evaporation process, and a 100 ns NPT MD production simulation. All simulations proceeded under 298 K and 1 bar in agreement with experimental environments. To model the solvent evaporation process, 200 random solvent molecules were evaporated in the time interval of 1 ns and 10 ns equilibrium was carried out after the completion. Then, it was annealed to 600 K and quenched back to 298 K to perform 100 ns NPT MD production process. The V-rescale thermostat and Berendsen barostat under the NPT ensemble were applied to

control the temperature and pressure. In the final MD production, the Parrinello-Rahman method was applied. The VMD software was used for the visualization.<sup>[10-11]</sup>

# 2.4 Test of contact angle and calculation of flory-huggins interaction parameters.

The surface energy  $\gamma$  values can be calculated for neat films according to the Wu model using the following equation:

$$\frac{4\gamma_L^d \gamma_S^d}{\gamma_L^d \gamma_S^d} + \frac{4\gamma_L^p \gamma_S^p}{\gamma_L^p \gamma_S^p}$$
[1]  
$$\gamma = \gamma^d + \gamma^p$$
[2]

The surface energy  $\gamma$  of the molecule acceptors and polymer donors was determined based on the testing of the two different contact angles of water and glycerol. The data is presented in the Figure S14 and Table S8, where  $\gamma$  represents the sum of dispersion (d) and polar (p) components. The solubility parameter  $\delta$  is proportional to the square root of  $\gamma$ , and then we can calculate the flory-huggins interaction parameter  $\chi$  according to the equation:

$$\chi_{ij} = \frac{V_1}{RT} (\delta_i - \delta_j)^2 + 0.34$$
[3]

The V<sub>1</sub> value is 79.5 cm<sup>3</sup> mol<sup>-1</sup> in the chloroform solution, and the  $\chi$  values of PM6 and L8-BO are shown in the Table S8. The flory-huggins parameter between PM6 and L8-BO is 0.39 K, while the flory-huggins parameter between PM6 and L8-BO treated with TZ-3Cl is 0.36 K. This indicates better miscibility, which is also a significant reason high PCE values.

### 3. Materials and synthetic routes

### Synthetic details and characterizations

Unless otherwise noted, all commercial chemicals were used without further purification. <sup>1</sup> H NMR and <sup>13</sup>C NMR spectra were recorded on a JEOL ECZ 400 MHz or 600 MHz spectrometer. The chemical shift ( $\delta$ ) values are given in ppm and are referenced to TMS or residual solvent peaks. **TZ-Cl** and **TZ-3Cl** were synthesized

through the following route.



Scheme S1. Synthetic routes of TZ-Cl and TZ-3Cl.

### 4-chlorothiazole (TZ-Cl)

Zinc dust (1.51 g, 22.98 mmol) was added to the solution of 2,4-dichlorothiazole (1.00 g, 6.49 mmol) in acetic acid (10 mL) and then the mixture was heated to reflux for 6 h. After cooled to room temperature, the solid was removed by filtration and was washed with acetic acid. The filtrate was poured into ice water (40 mL) and treated with about 50% (*w*/*v*) aqueous NaOH until a slightly alkaline mixture resulted (pH = 9). The mixture was extracted with diethyl ether (3 × 100 mL), and the combined organic phase was dried with anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to obtain 4-chlorothiazole as a colorless liquid (0.54 g, 70% yield). <sup>[12]1</sup>H NMR (400 MHz, Chloroform-*d*):  $\delta$  8.74 (d, 1H), 7.17 (d, 1H) ppm; <sup>13</sup>C NMR (151 MHz, Chloroform-*d*)  $\delta$  152.82, 140.65, 113.23 ppm. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>3</sub>H<sub>2</sub>NSC1 119.9669; Found 119.9673.

### 2,4,5-trichlorothiazole (TZ-3Cl)

Sulfuryl chloride (2.63 g, 19.48 mmol) was added dropwise to the stirring solution of 2,4-dichlorothiazole (1.00 g, 6.49 mmol) in CHCl<sub>3</sub> (5 mL). After stirring at 70 °C for 8 h, the mixture was cooled to room temperature and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel by

hexane to give **TZ-3Cl** as a colorless liquid (0.86 g, 70% yield). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  147.98, 135.64, 120.53 ppm. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>3</sub>HNSCl<sub>3</sub> 187.8890; Found 187.8894.

# <sup>1</sup>H NMR Experiments



Figure S1. The <sup>1</sup>H NMR spectra of L8-BO with or without TZ-3Cl in CDCl<sub>3</sub>.



![](_page_9_Figure_0.jpeg)

Figure S2. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of TZ-Cl in CDCl<sub>3</sub>.

![](_page_9_Figure_2.jpeg)

![](_page_9_Figure_3.jpeg)

![](_page_10_Figure_0.jpeg)

Figure S3. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of TZ-3Cl in CDCl<sub>3</sub>.

## **Supplementary Figures and Tables**

All samples below have undergone annealing treatment to ensure complete volatilization of additives.

**Table S1.** Optimization process of different additives and processing conditions inPM6: L8-BO OSCs.

Additive	Additive	Annealing	$V_{\rm oc}$ (V)	FF (%)	$J_{ m sc}$	PCE (%)
	Concentration	Temperature	. ,	. ,	$(mA/cm^2)$	
	0.1%	80 °C	0.89	72.04	26.82	17.29
		90 °C	0.90	73.09	26.93	17.65
		100 <sup>o</sup> C	0.88	74.06	26.96	17.60
	0.25%	80 °C	0.88	73.66	26.77	17.42
		90 °C	0.89	75.38	26.96	18.05
		100 <sup>o</sup> C	0.88	75.57	27.12	18.11
	0.5%	80 °C	0.88	75.68	26.88	17.91
TZ-Cl		90 °С	0.90	76.31	26.71	18.32
		100 <sup>o</sup> C	0.89	74.21	26.93	17.80
	0.75%	80 °C	0.89	75.12	26.80	17.92
		90 °C	0.90	74.63	26.74	17.96
		100 <sup>o</sup> C	0.88	76.11	27.00	18.08
	1%	80 °C	0.90	75.21	26.54	17.96
		90 °C	0.90	74.36	27.02	18.08
		100 <sup>o</sup> C	0.89	74.98	26.46	17.66
	2mg/mL	80 <sup>o</sup> C	0.90	74.11	26.23	17.45
		90 °C	0.91	73.82	26.68	17.83

	0				
	100 <sup>o</sup> C	0.90	74.02	26.54	17.54
5mg/mL	80 °C	0.89	75.19	26.65	17.86
	90 °C	0.90	76.31	26.75	18.28
	100 °C	0.89	74.89	27.21	18.19
7mg/mL	80 <sup>o</sup> C	0.90	75.05	27.20	18.27
	90 °C	0.90	75.93	27.01	18.48
	100 °C	0.89	75.06	26.85	18.02
9mg/mL	80 °C	0.88	74.69	26.32	17.30
	90 °C	0.90	74.91	26.95	18.17
	100 <sup>o</sup> C	0.90	75.12	27.01	18.26
11mg/mL	80 °C	0.89	76.32	26.58	18.05
	90 °C	0.89	75.12	26.56	17.76
	100 °C	0.88	74.65	27.10	17.80
0.1%	80 °C	0.90	74.92	26.62	17.94
	90 °C	0.90	76.64	26.97	18.63
	100 °C	0.90	76.91	26.81	18.62
0.25%	80 °C	0.90	76.60	26.76	18.48
	90 °C	0.91	76.63	27.11	19.11
	100 <sup>o</sup> C	0.91	76.23	26.89	18.57
0.5%	80 °C	0.91	79.60	26.43	19.18
	90 °C	0.90	80.19	27.29	19.80
	100 °C	0.90	77.90	27.07	19.03
0.75%	80 °C	0.90	79.00	26.89	19.12
	90 °C	0.91	78.91	27.01	19.40
	100 °C	0.91	78.02	27.10	19.24
1%	80 °C	0.89	78.36	27.00	18.83
	90 °C	0.91	77.96	26.98	19.14
	100 °C	0.90	78.35	26.77	18.88
	5mg/mL 7mg/mL 9mg/mL 11mg/mL 0.1% 0.25% 0.5% 0.5% 1%	100 °C           5mg/mL         80 °C           90 °C         100 °C           7mg/mL         80 °C           90 °C         100 °C           7mg/mL         80 °C           90 °C         100 °C           9mg/mL         80 °C           90 °C         100 °C           11mg/mL         80 °C           90 °C         100 °C           11mg/mL         80 °C           90 °C         100 °C           0.1%         80 °C           90 °C         100 °C           0.25%         80 °C           90 °C         100 °C           0.5%         80 °C           90 °C         100 °C           0.75%         80 °C           90 °C         100 °C           100 °C         100 °C           100 °C         100 °C	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table S2. Optimization process of 0.5% ( $\nu/\nu$ ) TZ-3Cl and processing conditions in

Sample	Annealing	Annealing	$V_{\rm oc}({ m V})$	FF (%)	$J_{\rm sc}({\rm mA/cm^2})$	PCE (%)
	Temperature	Time				
	80 °C	1min	0.90	75.24	26.93	18.19
		3min	0.91	79.60	26.43	19.18
		7min	0.91	76.44	26.21	18.16
TZ-3Cl	90 °C	1min	0.91	76.78	26.86	18.84
0.5%		3min	0.90	80.19	27.29	19.80
		7min	0.91	77.79	26.09	18.47
	100 °C	1min	0.91	76.97	26.52	18.50
		3min	0.90	77.90	27.07	19.03
		7min	0.90	76.64	26.45	18.24

PM6: L8-BO OSCs.

**Table S3.** Optimization process of 0.5% (v/v) **TZ-3Cl** and processing conditions in different D/A OSCs.

Sample	$V_{aa}(\mathbf{V})$	FF (%)	$J_{ac}(mA/cm^2)$	PCE (%)
PM6: BTP-eC9-4F (control)	0.85	73.71	28.01	17.58
<b>TZ-3Cl</b> $(0.5\% v/v)$	0.85	78.64	28.44	19.01
D18: BTP-eC9-4F (control)	0.88	72.82	26.67	17.09
<b>TZ-3Cl</b> (0.5%)	0.88	76.49	27.81	18.82

D18: L8-BO (control)	0.91	75.22	25.58	17.58
<b>TZ-3Cl</b> (0.5%)	0.92	79.55	26.90	19.61
PM6:Y6 (control)	0.83	73.26	26.56	16.24
<b>TZ-3Cl</b> (0.5%)	0.85	73.02	28.15	17.46
D18:Y6 (control)	0.84	67.78	27.78	15.74
<b>TZ-3Cl</b> (0.5%)	0.85	79.45	28.00	18.90

![](_page_12_Figure_1.jpeg)

**Figure S4.** The cyclic voltammograms of PM6 and L8-BO (a); The  $J^{1/2}-V$  characteristics of hole-only devices (b); The  $J^{1/2}-V$  characteristics (c) of electron-only devices by the space-charge-limited current (SCLC) method of different systems; Normalized PCE changes with time under room temperature (d), 60 °C (e) and constant light illumination (f). The process of decay of the photoelectric parameters of devices placed in a nitrogen glove box at room temperature over time (g, h, i), and the process of decay of the photoelectric parameters of devices placed on a 60 °C hot stage in a nitrogen glove box over time (j, k, l). The device used for stability testing at room temperature is ITO/2PACz/Polymer Donor: Acceptor/PDINN/Ag device structure, devices tested for stability under 60 °C and continuous light use ITO/ZnO/Polymer

Donor: Acceptor/MoO3/Ag device structure.

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Sample	$\mu_{\rm e} ({\rm cm}^2/{\rm Vs})$	$\mu_{\rm h}~({\rm cm^2/Vs})$	$\mu_{ m h}/\mu_{ m e}$
PM6:L8-BO (Control)	2.1 × 10 <sup>-4</sup>	3.1 × 10 <sup>-4</sup>	1.48
PM6:L8-BO (TZ-CI)	3.6 × 10 <sup>-4</sup>	$4.9 \times 10^{-4}$	1.36
PM6:L8-BO ( <b>TZ-2Cl</b> )	3.6 × 10 <sup>-4</sup>	5.3 × 10 <sup>-4</sup>	1.47
PM6:L8-BO ( <b>TZ-3Cl</b> )	6.2 × 10 <sup>-4</sup>	$7.5 \times 10^{-4}$	1.20

![](_page_13_Figure_3.jpeg)

**Figure S5.** The *J*-*V* curves (a); The EQE curves (b) and the EQE<sub>EL</sub> curves (c) of different systems.

![](_page_13_Figure_5.jpeg)

Figure S6. Normalized absorption and photoluminescence (PL) emission spectra of

![](_page_14_Figure_1.jpeg)

**Figure S7.** Normalized UV-vis absorption spectra of PM6:L8-BO blend films (a) and (b); TEM images of PM6:L8-BO blend films with/without additives (c).

![](_page_14_Figure_3.jpeg)

Figure S8. Statistics of fiber diameter of PM6:L8-BO blend films (with/without additive).

![](_page_15_Figure_0.jpeg)

**Figure S9.** The schematic diagram of peak fitting of OOP direction 1D GIWAXS curves, corresponding to the Figure 7b.

![](_page_15_Figure_2.jpeg)

**Figure S10.** 2D GIWAXS patterns (a, d) and 1D GIWAXS profiles (b, e) of L8-BO/PM6 (with/without additives); The schematic diagram of peak fitting of OOP direction 1D GIWAXS curves (c, f).

Sample	<b>010</b> (oop)								
	$q_{z}$ (Å <sup>-1</sup> )	$\pi$ - $\pi$ distance (Å)	FWHM (Å <sup>-1</sup> )	CCL (Å)					
PM6(Control)	1.63	3.85	0.32	17.46					
PM6( <b>TZ-3Cl</b> )	1.63	3.85	0.28	19.96					
L8-BO(Control)	1.72	3.65	0.29	19.28					
L8-BO(TZ-3Cl)	1.73	3.63	0.25	22.36					
PM6:L8-BO(Control)	1.68	3.74	0.29	19.28					

PM6:L8-BO(TZ-CI)	1.68	3.74	0.26	21.50
PM6:L8-BO( <b>TZ-2Cl</b> )	1.70	3.70	0.28	19.96
PM6:L8-BO(TZ-3Cl)	1.70	3.70	0.21	26.62

![](_page_16_Figure_1.jpeg)

Figure S11. The FT-IR spectra of PM6/L8-BO (a); PM6:L8-BO blend films (with/without additive) and TZ-3Cl (b).

![](_page_16_Figure_3.jpeg)

![](_page_17_Figure_0.jpeg)

**Figure S12.** TA results of PM6/L8-BO neat films and the corresponding GSB delay signal probed at 630/844 nm.

Materials	Pump Energy (µJ/cm <sup>2</sup> )	$n_0$ (×10 <sup>-17</sup> cm)	τ 1/2 (ps)	k (×10 <sup>9</sup> s <sup>-1</sup> )	α	$\gamma (\times 10^{-8} \text{ cm}^3 \text{s}^{-1})$	$D (\times 10^{-3} \text{ cm}^2 \text{s}^{-1})$	$\tau(\text{ps})$	L <sub>D</sub> (nm)
PM6 (Control)	2.36	1.92	18.80	36.87	-	-	-	444.96	-
	23.58	19.23	14.65	-	0.78	0.76	3.02	-	11.59
PM6 ( <b>TZ-Cl</b> )	2.36	2.67	20.90	33.16	-	-	-	481.50	-
	23.58	26.69	14.64	-	0.70	0.74	2.96	-	11.94
PM6 (TZ- 2Cl)	2.36	2.58	19.80	35.01	-	-	-	434.58	-
	23.58	25.76	13.70	-	0.69	0.85	3.38	-	12.12
PM6 (TZ- 3Cl)	2.36	1.88	18.90	36.67	-	-	-	401.18	
	23.58	18.76	13.65	-	0.72	1.05	4.19	-	12.97
L8-BO (Control)	0.19	0.64	34.50	20.09	-	-	-	281.84	-

Table S6. Detailed parameters of single exciton decay dynamic for films.

	3.83	12.81	5.85	-	0.17	11.00	43.76	-	35.12
L8-BO ( <b>TZ-Cl</b> )	0.19	0.64	34.75	19.95	-	-	-	394.22	-
	3.83	12.72	5.50	-	0.16	11.94	47.53	-	43.29
L8-BO (TZ- 2Cl)	0.19	0.62	44.80	15.47	-	-	-	421.36	-
	3.83	12.36	6.10	-	0.14	11.38	45.29	-	43.68
L8-BO (TZ- 3Cl)	0.19	0.63	29.55	23.45	-	-	-	423.68	
	3.83	12.63	5.50	-	0.19	11.62	46.22	-	44.25

![](_page_18_Figure_1.jpeg)

**Figure S13.** The chemical structure of BTP-eC9-4F and DM-F (a); The energy levels of BTP-eC9-4F and DM-F (b);<sup>[13]</sup> The *J-V* and EQE curves of PM6: BTP-eC9-4F:DM-F ternary OSCs with/without **TZ-3Cl**.

Active layer	$V_{\rm oc}$	$J_{ m sc}$	FF	$J_{ m calc}$	PCE (%)
	(V)	$(mA/cm^2)$	(%)	$(mA/cm^2)^{a}$	b
PM6:BTP-eC9-4F:DM-	0.897	27.32	77.50	26.71	19.0
F					(18.8)
1:1:0.2 (Control)					
PM6:BTP-eC9-4F:DM-	0.902	28.01	79.83	26.92	20.2
F 1:1:0.2 (0.5% <b>TZ-</b>					(19.9)
3Cl)					~ /

**Table S7.** PM6-based OSCs photovoltaic characteristics under simulated AM 1.5 G (100 mW/cm<sup>2</sup>) illumination.

<sup>a</sup> The  $J_{calc}$  was calculated from the EQE spectra and <sup>b</sup> average PCE was obtained by 8 devices.

![](_page_19_Figure_3.jpeg)

Figure S14. The contact angles of PM6 and L8-BO.

**Table S8.** Contact angle of water and glycerol, surface tension and Flory-Huggins Interaction Parameters for acceptors and donor.

	Film	Constact angle (°)		$\gamma^{d}$	$\gamma^{\mathrm{p}}$	γ	δ	$\chi(K)$
		water	glycero	(mN/m)	(mN/m)	(mN/m)		
Control	PM6	98	73	23.55	3.70	27.25	9.55	0.39
	L8-BO	90	64	22.00	1.73	23.73	8.91	
TZ-3Cl	PM6	102	72	29.71	0.22	29.93	10.01	0.36
	L8-BO	92	65	25.10	2.70	27.80	9.65	

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