## **Supporting Information**

# Constructing efficient organic solar cells by highly volatile solid additives with controlled phase morphology

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### **Experiment and materials**

#### 1.Materials

D18, L8-BO and PDINN were synthesized in lab according to literatures. Chloroform and methanol were purchased from Sigma-Aldrich. Poly(3,4 ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was sourced from Heraeus. Other chemical reagents were from commercial supplies and could be used directly unless otherwise specific instructions.

#### **2.Synthetic Section**



Scheme. 1 Synthesis routes of (a) TFT and (b) PT.

#### 2- (3,4,5-trifluorophenyl) thiophene (TFT) (a)

5-bromo-1,2,3-trifluorobenzene (2g, 9.48mmol), thiophene-2-boronic acid pinacol ester (2.99g, 14.2mmol), NaHCO<sub>3</sub> (7.97g, 94.8mmol) were dissolved in 50ml of THF and 10ml of H<sub>2</sub>O in a 250ml flask under inert atmosphere. Then the catalyst  $Pd_2(dba)_3$  (173.6mg, 0.02mmol) and the ligand P(O-Tol)<sub>3</sub> (115.6mg, 0.04mmol) were added. The mixture was stirred and refluxed for 16 hours under nitrogen protection. After cooling the reactant to room temperature and then the crude product was extracted and evaporating the solvent. Then purified by silica gel column chromatography with PE as eluent and methanol recrystallization. Finally, white solid product was gained with a yield of 80%.<sup>1</sup>

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 5.1Hz, 1H), 7.26 (d, *J* = 2.5Hz 1H), 7.23 – 7.18 (m, 2H), 7.09 (dd, *J* = 5.1, 3.6 Hz 1H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 152.49, 150.83, 141.26, 140.14, 138.41, 130.85, 128.55, 126.42, 124.63, 110.14.

#### 2-phenylthiophene (PT) (b)

Synthesis follows the same conditions as (a), using bromobenzene instead of 5-bromo-1,2,3-trifluorobenzene. Finally, white solid product was gained with a yield of 85%.

<sup>1</sup>H NMR (600 MHz, Chloroform-d) δ 7.63 (d, *J* = 7.5Hz, 2H), 7.39 (t, *J* = 7.7Hz, 2H), 7.33 (d, *J* = 4.4Hz, 1H), 7.32 – 7.27 (m, 2H), 7.10 (dd, *J* = 5.1, 3.6 Hz, 1H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 144.65, 134.61, 129.09, 128.21,

127.67, 126.17, 125.02, 123.28.

#### **3.**Solution preparation

D18 and L8-BO were synthesized in lab. The solution of D18:L8-BO (1:1.2) with PT or TFT in chloroform (CF) was stirred at 50°C for 60 min in N2-filled glovebox. The concentration of D18 and additives were 4.7 and 2mg/mL, respectively.

#### **4.Devices fabrication**

A conventional structure of indium-doped tin oxide (ITO)/poly(3,4ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS)/active layer/PDINN /Ag was applied. The pre-cleaned ITO glasses were treated by UV-ozone for 30 min. The PEDOT: PSS solution was deposited onto the pre-cleaned ITO substrates followed by annealing at 150 °C for 20 min. The solution of photovoltaic materials was spin-coated onto the PEDOT: PSS film in N2-filled glove box (annealing at

100 °C of 1 min). Then PDINN (Derthon)/methanol (1mg/mL) was spincoated accordingly. Finally, 100 nm Ag was thermally evaporated through a shadow mark at a vacuum pressure below  $3 \times 10^{-6}$  Torr. The effective area for each cell was 0.04 cm<sup>2</sup>.

#### 5. characterization.

The UV-visible absorption spectra were obtained on a PerkinElmer UVvis spectrometer model Lambda 750. AFM measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. H and C NMR spectra were recorded on Bruker AV 400 spectrometer . The J-V curve of the device was tested using an instrument from Enli Technology Ltd., Taiwan (SS-F53A) under AM 1.5G AAA light source with 100 mW/cm2 light intensity. EQE measurements were performed using a solar cell spectral response measurement system (QER3011, Enli Technology Co. Ltd), and the intensity was calibrated with a standard single crystal Si photovoltaic cell.<sup>2</sup>

#### **GIWAXS** characterization

GIWAXS data were obtained at 1W1A Diffuse X-ray Scattering Station, Beijing Synchrotron Radiation Facility (BSRF-1W1A). The monochromatic of the light source was 1.54 Å. The data were recorded by using the two-dimensional image plate detector of Eiger 2M from Dectris, Switzerland.

#### Charge mobility measurement by SCLC method

The architectures of ITO/ZnO/Active layer/PDINN/Ag and ITO/PEDOT:PSS/Active layer/MoO<sub>3</sub>/Ag were used for electron and hole mobility measurement, respectively. The mobilities were calculated according to the Mott-Gurney equation:  $J = 9\varepsilon\varepsilon_0\mu/(8L^3)V^2$ , where J is the current density;  $\varepsilon$  is the dielectric constant of the blend film;  $\varepsilon_0$  is the permittivity of the vacuum;  $\mu$  is the mobility; L is the thickness of the film;  $V = V_{appl} - V_{bi}$ ,  $V_{appl}$  and  $V_{bi}$  are the applied voltage to the device and the build-in voltage, respectively.

#### J-V and EQE Measurement

The J-V curves of the devices were measured in a glove box with an instrument from Enli Technology Ltd., Taiwan (SS-F53A) under AM 1.5G illumination (AAA class solar simulator, 100 mW cm<sup>-2</sup> calibrated with a standard single crystal Si photovoltaic cell). EQE measurements were performed by a solar cell spectral response measurement system (QER3011, Enli Technology Co. Ltd), and the intensity was calibrated with a standard single-crystal Si photovoltaic cell before the test.

## Supplementary Fig.



Fig. S1. The UV-Vis absorption spectra of (a) DI8:L8-BO films (b) D18





Fig. S2. Contact angle images of D18, L8-BO, PT and TFT films with water and glycerol.



Fig. S3. ESP distribution of D18 and L8-BO.



**Fig. S4.** 2D GIWAXS patterns of (a-c) D18 films (d-f) L8-BO without and with different additives.



**Fig. S5.** 1D GIWAXS line-cut profile of D18 films without and with different additives. The solid and dash lines represent the line-cut profile of OOP and IP directions.



**Fig. S6.** The curves of (a) D18:L8-BO based devices with different additives TFT concentrations.



Fig. S7. EQE curves of (a) DI8:L8-BO based devices without and with different additives.

Table S1. Summary of contact angles ( $\theta$ ), surface tensions ( $\gamma$ ), Flory-Huggins interaction parameters  $(\chi)$ , and Wetting coefficient  $(\omega)$  for various films.

Sample	$ heta_{ m water}$ (deg)	$ heta_{ m GL}$ (deg)	$\gamma^{d}$ [mJ.m <sup>-1</sup> ]	γ <sup>p</sup> [mJ.m <sup>-1</sup> ]	$\gamma$ [mJ.m <sup>-1</sup> ]	σ
D18	107.07	93.48	14.98	1.15	16.13	7.35
L8-BO	95.87	82.64	18.33	3.16	21.49	8.48
РТ	89.33	74.21	23.35	3.99	27.34	9.57
TFT	83.93	73.62	17.84	8.26	26.11	9.35

Table S2	• A summary	of <i>a</i> -spacing	and	conerence	lengths	(CCL)	01
blend L8-	BO without and	d with additive	es.				
	In	plane		Ou	it of plar	ne	

Table	<b>S2.</b> <i>A</i>	A summary	of <i>d</i> -spacing	and	coherence	lengths	(CCL)	of
blend I	L8-BC	D without and	d with additive	es.				
			1		0	0 1		

	In plane			Out of plane		
	<i>Q</i> (Å <sup>-1</sup> )	d- spacing (Å)	CCLs( Å)	<i>Q</i> (Å <sup>-1</sup> )	<i>d</i> - spacing (Å)	CCLs( Å)
L8-BO	0.47	13.4	78.54	1.71	3.67	29.76
L8- BO:PT	0.35	18.0	31.42	1.72	3.65	31.42

L8-	0.45	14.0	80.22	1 72	2 65	25 24
BO:TFT	0.45	14.0	80.22	1.72	5.05	55.54

**Table S3.** A summary of *d*-spacing and coherence lengths (CCL) of blend D18 without and with additives.

-	In plane			Out of plane		
	Q (Å -1)	d- spacing (Å)	CCLs( Å)	<i>Q</i> (Å <sup>-1</sup> )	<i>d</i> - spacing (Å)	CCLs ( Å)
D18	0.31	20.20	55.34	1.67	3.76	25.24
D18:PT	0.31	20.27	56.46	1.68	3.73	25.96
D18:TFT	0.31	20.29	56.46	1.67	3.76	25.54

Table S4. A summary of *d*-spacing and coherence lengths (CCL) of

blend D18:L8-BO without and with additives.

	In plane			Out of plane		
	<i>Q</i> (Å <sup>-1</sup> )	<i>d</i> - spacing (Å)	CCLs ( Å)	Q (Å -1)	d- spacing (Å)	CCLs ( Å)
D18:L8- BO	0.2975	21.11	65.62	1.615	3.89	37.69
D18:L8- BO:PT	0.300	20.94	68.16	1.615	3.89	39.47
D18:L8- BO:TFT	0.300	20.94	68.47	1.615	3.89	40.05

Table S5. The photovoltaic parameters of D18:L8-BO devices with

different TFT	concentrations.
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TFT	$V_{\rm OC}$ (V)	$J_{ m SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
0	0.925	25.46	75.08	17.70
2mg/ml	0.912	26.20	79.69	19.19
4mg/ml	0.913	25.85	75.99	17.95

6mg/ml	0.890	25.17	75.31	16.85
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 Table S6. The charge mobilities of D18:L8-BO blend films without and

 with additives.

D18:L8-BO	$\mu_{e} \times 10^{-4}$ cm <sup>2</sup> v <sup>-1</sup> s <sup>-1</sup>	$\mu_{\rm h} \times 10^{-4}$ cm <sup>2</sup> v <sup>-1</sup> s <sup>-1</sup>	$\mu_{\rm e}/\mu_{\rm h}$
Control	4.23	2.27	1.86
РТ	5.53	3.35	1.65
TFT	7.15	5.73	1.24

 Table S7. The parameters of exciton dissociation efficiency and charge

D18:L8- BO	J sat (mA/cm <sup>2</sup> )	$J \mathrm{ph}$ (mA/cm <sup>2</sup> )	$J \max$ (mA/cm <sup>2</sup> )	$P_{\rm diss}(\%)$	$P_{\text{coll}}(\%)$
Control	26.06	25.07	21.67	96.20%	83.15%
РТ	26.87	26.26	24.68	97.73%	91.85%
TFT	26.87	26.06	24.81	96.99%	92.33%

collection efficiency of D18:L8-BO devices without and with additives.

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2. B. Zhang, N. An, H. Wu, Y. Geng, Y. Sun, Z. Ma, W. Li, Q. Guo and E. Zhou, *Sci. China* : *Chem.*, 2020, **63**, 1262-1271.