# **Supporting information**

#### Fluorinated solid additives enable high efficiency non-fullerene organic solar cells

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### **1. Experimental Section**

#### Materials

PBDB-T-2F was purchased from Solarmer Materials (Beijing) Inc. BTP-4F was purchased from eFlex PV Technology (Shenzhen) Co., ltd. ZnO precursor was synthesized according to a previous report.<sup>1</sup> Other reagents and solvents were purchased from commercial sources and used as received. INB-1F, INB-3F and INB-4F were synthesized with Knoevenagel condensation reactions between 1H-indene-1, 3(2H)-dione and fluorinated benzaldehyde derivatives, with details described in the supporting information. (Scheme S1 in the support information, SI).

### **Fabrication of Organic Solar Cells**

Solar cell devices were fabricated with an inverted structure. The pre-patterned ITO-glass (resistance ca. 15  $\Omega$  sq<sup>-1</sup>) were cleaned by ultra-sonication in water, ethanol, and isopropyl alcohol for 10 mins each. Then these substrates were further treated with ultraviolet/ozone for another 15 mins after drying at 100 °C on a hotplate to remove any organic contaminants. ZnO films were

spin-coated at 3000 rpm from the ZnO precursor solution, followed by thermal annealing at 200 °C for 30 mins and the final film thickness was *ca.* 30 nm. For the fabrication of PBDB-T-2F:BTP-4F (1:1.2 mass ratio) OSCs, the active layer solutions were prepared in chloroform with a total solid concentration of 16 mg/mL. The additives (mole ratio of NFA:additive varied) were added into the donor:acceptor solution and stirred for another 30 mins. Then the blend solution were spin-coated onto the ZnO layer in an N<sub>2</sub> glovebox at 3200 rpm, followed by thermal annealing at 110 °C for 10 mins to obtain films of *ca.* 120 nm thickness. For the PBDB-T-2F:IT-4F (1:1 mass ratio) OSCs, the active layer was deposited onto ZnO by spin-coating at 1600 rpm from a 10 mg/ml chloroform solution, then dried at 160 °C for 30 mins. The final film thickness is *ca.* 100 nm. Finally, 10 nm MoO<sub>3</sub> and 100 nm Ag were thermally evaporated through shadow masks under high vacuum to form the hole transport layer and the anode, respectively. The size of the active area for OSCs defined by shadow mask is 4 mm<sup>2</sup>.

#### **Instruments and Measurements**

A Bruker Avance III HD 500 MHz spectrometer was used to measure the <sup>1</sup>H and <sup>13</sup>C NMR spectra of all compounds. The current density-voltage (J-V) curves of solar cell devices were tested at room temperature with a Newport 3A solar simulator under AM 1.5G (100 mW cm<sup>-2</sup>), of which the light intensity has been calibrated with a silicon solar reference cell certified by the National Renewable Energy Laboratory (NREL, USA). Device J-V characteristics were obtained with J-V sweep software developed by Ossila Ltd. (Sheffield, UK) and a Keithley 2612B source meter unit. A metal aperture mask was covered above the devices to accurately define an area of 2.12 mm<sup>2</sup> for each device, which can eliminate the influence of any edge effects. The stability tests of the optimized PBDB-T-2F:BTP-4F OSCs were performed under the same ambient conditions (with an average temperature of 25 °C and humidity around 70%). External quantum efficiency (EQE) was carried out using a Zolix system (China) equipped with a standard Si diode and the monochromatic beam was generated using a 150 W xenon lamp. Film absorption spectra were carried out using a UV-Visible spectrophotometer (HITACHI, Japan). Film thickness was measured using a spectroscopic ellipsometer (J. A. Woollam, USA). The surface morphology of photovoltaic films was characterized by an atomic force microscope (Solver Next, NT-MDT, Russia) with AFM probes using ETALON Series HA NC (Scansens GmbH, Ostec Group, Germany). Synchrotron grazing-incidence small-angle X-ray scattering measurements were carried out using the beamline BL16B1 at the Shanghai Synchrotron Radiation Facility in China. Grazing-incidence wide-angle Xray scattering measurements were performed at the University of Sheffield, UK. The GIWAXS Xray measurements were performed using a Xeuss 2.0 (XENOCS, France) laboratory machine. The system is equipped with a MetalJet (Excillum, Sweden) liquid gallium X-ray source, providing a 9.24 keV X-ray beam. Films were prepared on Si substrates and an incidence angle of 0.16° was used for the X-ray measurements, with data reduction and analysis using the GIXSGUI MATLAB toolbox.<sup>2</sup>

The space charge-limited current (SCLC) method based the Mott-Gurney equation:  $J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{V^3}$ 

 $8^{\circ r \circ_0 r} L^3$  was used to study the electron and hole mobilities. The devices with structures of ITO/ZnO/Active layer/Ca/Ag and ITO/PEDOT:PSS/Active layer/MoO<sub>3</sub>/Ag were fabricated, respectively. Where J is the current density,  $\varepsilon_r$  is the relative dielectric constant of active layer material usually 2-4 for organic semiconductor, herein we use a relative dielectric constant of 3,  $\varepsilon_0$  is the permittivity of empty space,  $\mu$  is the mobility of hole or electron and L is the thickness of the active layer, V is the internal voltage in the device, and  $V = V_{app}-V_{bi}$ , where  $V_{app}$  is the voltage applied to the device, and  $V_{bi}$  is the built-in voltage resulting from the relative work function difference between the two electrodes.<sup>3</sup>

#### **Molecular Dynamics Simulations**

Molecular dynamics simulations were performed to determine the interactions among molecules (electron acceptor BTP-4F and additives), through the software Materials Studio 2017. The Forcite and DMol3 modules were used to optimize the geometry of the acceptor and additives separately. In the Forcite module, the Compass II forcefield was used to assign charges, and the atom-based summation method was used to determine the electrostatic and van der Waals interactions. The results from Forcite was further processed to obtain geometry optimization in the DMol3 module using the generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof(PBE) functions. The electrostatic potential (ESP) mapped figures and torsion angles of additives were obtained using energy task in the DMol3 module. Then the optimized BTP-4F and additive molecules were put in the Adsorption Locator module to determine the adsorption sites of adsorbate on substrate. Firstly, one additive molecule adsorption on the BTP-4F and two

additive molecules on one BTP-4F surface was simulated to evaluate the molecular packing among BTP-4F molecules and the influence of additives. The geometry optimization and energy tasks were used to obtain the adsorption energy of various additives and BTP-4F in the Forcite module.

#### 2. Synthesis of INB-1F, 3F, 5F

#### Phthalicanhydride (compound 2)

Labelled phthalic acid (5 g, 30.1 mmol) was suspended in dichloromethane (5 ml) and heated under reflux with acetic anhydride (18 ml) for 3 h at 80 °C, the reaction mixture was subsequently allowed to cool down to room temperature and the volatile materials were evaporated under vacuum. <sup>4-5</sup> The crude product was purified through silica gel (400 mesh) column chromatography using ethyl acetate/petroleum ether (1/5, v/v) as the eluent to provide a colorless viscous liquid (3.73 g, 83.7% yield) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (dd, *J* = 5.6, 3.1 Hz, 2H), 7.92 (dd, *J* = 5.6, 3.0 Hz, 2H).

#### 1H-indene-1, 3(2H)-dione (compound 3)

To a solution of compound **2** (0.74 g, 5 mmol) in acetic anhydride (5 mL), triethylamine (2.5 mL) and ethyl acetoacetate (0.72 g, 5.5 mmol) were added dropwise under argon.<sup>6-7</sup> After stirring at room temperature overnight, and the reaction mixture was poured dropwise into a mixed solution of concentrated HCl and ice-water (about 20 ml, mass ratio 1:1) in portion. Then an extra concentrated HCl (10 ml, 5 M) was added into the above solution before being allowed to stir for another half an hour at room temperature. After that, the solution was refluxed for additional 2 h. After cooling down to room temperature, the solution was extracted with CHCl<sub>3</sub>, and the combined organic phase was dried over anhydrous Na<sub>2</sub>SO4. After removing the solvent under reduced pressure, the crude product was purified through silica gel column by eluting with ethyl acetate/petroleum ether(1/10, v/v) to obtain compound **3** as a grey-green solid (0.44 g, 60.4%) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (dd, J = 5.3, 3.2 Hz, 2H), 7.85 (dd, J = 5.4, 3.1 Hz, 2H), 3.25 (s, 2H).

### 2-(4-fluorobenzylidene)-1H-indene-1, 3(2H)-dione (INB-1F)

To a mixed solution of 4-fluorobenzaldehyde (1.24 g, 10 mmol),1H-indene-1, and 3(2H)-dione (1.46 g, 10mmol) in absolute ethyl alcohol (50 ml) was added piperidine (85.15 mg, 1 mmol). The mixture was allowed to stir and reflux at 60 °C for 3 h. After cooling down to room temperature, the precipitate was filtered and washed with EtOH. The residue was further purified using column

chromatography on silica gel employing CH<sub>2</sub>Cl<sub>2</sub> as an eluent to afford a pure yellow solid (1.38 g, 55%) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.57 – 8.44 (m, 2H), 7.97 (s, 2H), 7.80 (s, 3H), 7.16 (t, J = 8.1 Hz, 2H). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -103.4 (s). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  190.2 (s), 189.2 (s), 166.7 (s), 164.6 (s), 145.5 (s), 142.5 (s), 140.1 (s), 137.0 (d, *J* = 9.3 Hz), 135.5 (s), 135.3 (s), 129.6 (d, *J* = 3.1 Hz), 128.7 (s), 123.4(d, *J* = 2.4 Hz), 116.2 (s), 116.1 (s). EI-HRMS (TOF) m/z calcd for [M]<sup>+</sup> C<sub>16</sub>H<sub>9</sub>FO<sub>2</sub> 252.0661, found 252.0673.

### 2-(2,4,6-trifluorobenzylidene)-1H-indene-1, 3(2H)-dione (INB-3F)

Piperidine (150 mg, 1.76 mmol) was added into the ethyl alcohol (30 ml) solution of 2, 4, 6trifluorobenzaldehyde (0.8 g, 5 mmol) and 1H-indene-1,3 (2H)-dione (0.73 g, 5 mmol). The solution was refluxed at 60 °C for 3 h. After the reaction has finished, the precipitate was filtered. The residue was washed with ethyl alcohol and further purified through column chromatography employing CH<sub>2</sub>Cl<sub>2</sub> as an eluent to afford a pure yellow solid (0.63 g, 43.8%) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (d, *J* = 8.4 Hz, 1H), 7.98 (t, *J* = 3.9 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.73 (s, 1H), 6.78 (t, *J* = 8.2 Hz, 2H). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -102.5 (p, *J* = 8.8 Hz), -102.9 (t, *J* = 8.6 Hz). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  188.4 (s), 187.4 (s), 142.7 (s), 140.7 (s), 135.9 (s), 135.6 (s), 133.8 (s), 128.4 (s), 123.8 (s), 123.6 (s), 100.9 (s), 100.7 (s), 100.5 (s). EI-HRMS (TOF) m/z calcd for [M ]<sup>+</sup> C<sub>16</sub>H<sub>7</sub>F<sub>3</sub>O<sub>2</sub> 288.0463, found 288.0494.

#### 2-((perfluorophenyl) methylene)-1H-indene-1, 3(2H)-dione (INB-5F)

2, 3, 4, 5, 6-pentafluorobenzaldehyde (0.98 g, 5 mmol) and 1H-indene-1, 3(2H)-dione (0.73 g, 5 mmol), piperidine (150 mg, 1.76 mmol) ethyl alcohol (30 ml) were dissolved in a round bottom flask. The mixture was refluxed at 60 °C for 3 h. When it cooled to room temperature, the precipitate was filtered and washed by EtOH. The residue was recrystallized with CH<sub>2</sub>Cl<sub>2</sub> to give the light yellow solid (0.42 g, 25.9%) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.12 – 8.08 (m, 1H), 8.06 – 8.01 (m, 1H), 7.93 – 7.87 (m, 2H), 7.66 (s, 1H). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -135.0 (dt, *J* = 18.5, 7.6 Hz), -149.9 (t, *J* = 20.7 Hz), -161.6 (s). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  187.5 (s), 186.8 (s), 142.7 (s), 140.8 (s), 136.2 (s), 136.1 (s), 135.5 (s), 125.4 (s), 123.9(d, *J* = 18.2 Hz). EI-HRMS (TOF) m/z calcd for [M]<sup>+</sup> C<sub>16</sub>H<sub>5</sub>F<sub>5</sub>O<sub>2</sub> 324.0214, found 324.0417.



Scheme S1. Synthetic routes of INB-1F, 3F, 5F

3. The UV-Vis spectra of the INB-1F, 3F, 5F films before and after thermal annealing



Fig. S1. The absorption of pure INB-1F, 3F, 5F films with/without thermal annealing.



#### 4. Optimization of INB-1F content and annealing temperature in PBDB-T-2F:BTP-4F OSCs

**Fig. S2.** (a) J-V characteristics of OSCs processed with INB-1F at different mole ratio to BTP-4F, and (b) by thermal annealing at different temperatures.

**Table S1** Device metrics of PBDB-T-2F:BTP-4F OSCs processed with differentvolume of additives and after annealing at different temperatures. The standard deviations wereobtained from 20 devices.

BTP:INB-1F	Thermal	V <sub>OC</sub>	J <sub>SC</sub>	FF	PCE
ratio	annealing	[V]	$[mA cm^{-2}]$	[%]	[%]
BTP-4F:INB-1F (1:0.0)	N/A	0.82±0.00	26.4±0.3	70.0±0.3	15.1±0.1(15.2)
BTP-4F:INB-1F (1:0.2)	N/A	0.82±0.00	26.7±0.2	69.9±0.2	15.3±0.1(15.3)
BTP-4F:INB-1F (1:0.5)	N/A	0.82±0.00	27.0±0.2	70.0±0.2	15.5±0.2(15.6)
BTP-4F:INB-1F (1:1.0)	N/A	0.80±0.00	27.1±0.1	69.6±0.3	15.1±0.1(15.2)
BTP-4F:INB-1F (1:0.0)	90 °C	0.83±0.00	26.2±0.3	70.0±1.3	14.9±0.1(15.0)
BTP-4F:INB-1F (1:0.5)	90 °C	0.83±0.00	26.4±0.2	70.7±0.2	15.5±0.1(15.6)
BTP-4F:INB-1F (1:0.0)	110 °C	0.81±0.00	26.4±0.3	70.0±1.3	15.1±0.1(15.2)
BTP-4F:INB-1F (1:0.5)	110 °C	0.81±0.00	27.1±0.2	72.2±0.2	15.8±0.0(15.8)
BTP-4F:INB-1F (1:0.0)	130 °C	0.81±0.00	26.0±0.3	69.8±1.3	14.7±0.1(14.8)
BTP-4F:INB-1F (1:0.0)	130 °C	0.81±0.00	26.7±0.2	69.4±0.2	15.0±0.2(15.1)



**Fig. S3.** (a) Absorbance of the PBDB-T-2F:IT-4F films processed without and with solid additives and further treated with thermal annealing. (b) J-V characteristics and (c) EQE spectra of the corresponding PBDB-T-2F:IT-4F devices.

**Table S2** Device metrics of PBDB-T-2F:IT-4F OSCs processed without/with different additives.

 The standard deviations were obtained from 20 devices.

Component	V <sub>OC</sub> [V]	$J_{SC}$ [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
PBDB-T-2F:IT-4F	0.84±0.01	19.7±0.3	72.8±2.2	12.1±0.1(12.2)
PBDB-T-2F:IT-4F (INB-1F)	0.83±0.00	21.2±0.1	72.9±0.8	12.8±0.2(13.0)
PBDB-T-2F:IT-4F (INB-3F)	0.83±0.01	21.3±0.4	73.0±0.3	12.9±0.1(13.1)
PBDB-T-2F:IT-4F (INB-5F)	0.83±0.01	21.5±0.3	73.8±0.4	13.2±0.2(13.4)



**Fig. S4** (a) Electron current density versus bias voltage of the ITO/ZnO/Active layer/Ca/Ag electron-only devices and (b) hole current density versus bias voltage of the ITO/PEDOT:PSS/Active layer/MoO3/Ag hole- only devices.



**Fig. S5** (a) Voc versus light intensity and (b) Jsc versus light intensity of PBDB-T-2F:BTP-4F OSCs prepared with and without additives. The slope gradients are indicated in brackets.

**Table S3** The electron and hole mobilities of PBDB-T-2F:BTP-4F devices processed without/with different solid additives.

Component	$\mu_{e}$ (cm <sup>2</sup> ·V <sup>-1</sup> ·s <sup>-1</sup> )	$\mu_h  (cm^2 \cdot V^{-1} \cdot s^{-1})$	$\mu_e\!/\mu_h$
PBDB-T-2F:BTP-4F	5.9×10 <sup>-4</sup>	1.6×10 <sup>-4</sup>	3.7
PBDB-T-2F:BTP-4F (INB-1F)	6.9×10 <sup>-4</sup>	2.5×10 <sup>-4</sup>	2.8
PBDB-T-2F:BTP-4F (INB-3F)	7.4×10 <sup>-4</sup>	2.7×10 <sup>-4</sup>	2.7
PBDB-T-2F:BTP-4F (INB-5F)	7.9×10 <sup>-4</sup>	3.2×10 <sup>-4</sup>	2.5

#### 5. Surface morphology



**Fig. S6** The AFM height images of PBDB-T-2F:BTP-4F blend films processed without and with three different solid additives.

#### 6. Molecule dynamics simulations

The additive absorption energy  $E_{ad}$  (additive) is defined according to Equation 1:

$$E_{ad}(additive) = E_{(BTP - 4F/additive)} - E_{BTP - 4F} - E_{additive}$$
(1)

where three different terms on the right represent the system energy of BTP-4F/additive, BTP-4F, and additive, respectively. The absorption energy of three BTP-4F molecules on another BTP-4F surface were determined using Equation 2:

$$E_{ad}(3BTP - 4F) = E_{(BTP - 4F + 2additive/3BTP - 4F)} - E_{3BTP - 4F} - E_{(BTP - 4F + 2additive)}$$
(2)

where the three terms on the right are the system energy of one BTP-4F adsorbing three BTP-4F with the presence of two additive, three BTP-4F, and one BTP-4F with two additive molecules.

	E <sub>(BTP-4F/additive)</sub> (kcal/mol)	E <sub>(BTP-4F)</sub> (kcal/mol)	E <sub>(additive)</sub> (kcal/mol)	E <sub>ad</sub> (additive) (kcal/mol)	Average stacking distance between BTP-4F and additive (Å)
BTP-4F/INB-1F	347.1	351.8	29.1	-33.8	3.2
BTP-4F/INB-3F	340.6	355.7	18.0	-33.1	3.1
BTP-4F/INB-5F	348.6	352.2	34.9	-38.5	2.7

Table S4 Parameters of one BTP-4F molecule adsorbing one INB-1F, INB-3F, INB-5F molecule.

	E <sub>(BTP-4F+2additive</sub> /3BTP-4F (kcal/mol)	E <sub>(3BTP-4F)</sub> (kcal/mol)	E <sub>(BTP-4F+2additive)</sub> (kcal/mol)	E <sub>ad</sub> (3BTP-4F) (kcal/mol)	Average stacking distance between BTP-4F
					(Å)
BTP-4F/3BTP-4F	1205.8	995.5	362.4	-152.1	3.6
(BTP-4F+2INB-1F) /3BTP-4F	1202.5	1011.5	394.8	-203.8	3.4
(BTP-4F+2INB-3F) /3BTP-4F	1201.3	1018.6	385.4	-202.7	3.4
(BTP-4F+2INB-5F) /3BTP-4F	1232.4	1024.1	414.0	-205.7	3.4

**Table S5** Parameters of three BTP-4F molecules absorbing onto one BTP-4 molecules withoutadditives or with the presence of two INB-1F, INB-3F, INB-5F molecules.

7. Nuclear magnetic resonance spectroscopy











#### -131, 99 -101, 99 -101, 90 -10



INB-5F <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)



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