## Revealing the role of solvent additives on morphology and energy loss in

# benzodifuran polymer based non-fullerene organic solar cells

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### Synthesis of PBDF-BDD

M1 and M2 were synthesized according to reported literature, respectively. M1 (0.2 mmol) and M2 (0.2 mmol) was mixed in 5 mL of toluene, and then the solution was purged with argon for 5 min. The catalyst, Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mg), was added in one portion, and the mixture was purged with argon for another 20 min. The reaction was then stirred at 110 °C for 6 h under argon protection. The polymer solution was cooled to room temperature and precipitated from 50 mL of methanol then collected by filtration and then subjected to Soxhlet extraction with methanol, hexane, and chloroform in the end. The polymers were recovered as solid from the chloroform fraction by precipitation from methanol, and collected as metallic purple solid with a yield of 60% after dry in under vacuum.  $M_n$ : 13.85 kDa,  $M_w$ : 28.81 kDa.



Scheme S1. The synthetic route of PBDF-BDD.

#### **Experimental Section**

*Device Fabrication:* The BDF based devices were fabricated with inverted device structure of ITO/ZnO/active layer (120nm) /MoO<sub>x</sub>/Ag. Indium tin oxide (ITO) covered glasses were cleaned by an ultrasonication treatment in detergent, ultrapure water, ethanol, acetone, and ethanol every 30 min, and then dried with air blow. For active layer of BDF based donor blend with IT-4F in a ratio of 1:1in CF solvent, and maintain

a concentration of 18mg/ml with different additives inside. These precursors were stirred in nitrogen-filled glove box for 8h. Then spin-coated on ZnO layer. After annealing at 130 °C for 2min, hole transport layer  $MoO_x(1.5nm)$  and electrode Ag(100nm) were formed via vacuum evaporation.

*Measurement:* All the measurements were carried out under ambient condition. The current-voltage (J-V) characteristics of the devices were measured on a Keithley 2400 Source Measure Unit. The power conversion efficiency (PCE) was measured under an illumination of AM 1.5G (100 mW/cm<sup>2</sup>) using a 7IS0503A (SOFN Instruments Co. Ltd.) solar simulator. The EQE was measured by 7-SCSpec (SOFN Instruments Co. Ltd.) which light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The morphologies of the polymer/acceptor were investigated by AFM (Dimension Fastscan) in contacting under normal air conditions at room temperature with 2µm scanner.

Electroluminescence measurements were done using a source meter (Keithley 2400) to inject electric current, and the emitted photons were measured using a fluorescence spectrometer (KYMERA-3281-B2, Andor) with two sets of diffraction gratings, a Si EMCCD camera (DU970PBVF, Andor) for the wavelength range of 400~1000 nm, and an InGaAs camera (DU491A-1.7, Andor) for the wavelength range of 900~1600 nm. Photoluminescence measurements were done using a laser excitation (460 nm), and the emission spectra were obtained using the same setup used for recording electroluminescence spectra. The transient photovoltage decay measurements were done using two white LED lamps, driven by a Keithley 2450 source meter for different

bias illumination intensities and an arbitrary function generator (AFG3022C, Tektronix) for the transient illumination. The peaks of the transient voltage signals, recorded by an oscilloscope (MDO4104C, Tektronix), were kept to approximated 5% of the DC bias photovoltage signal, by adjusting the driving voltage of the LED controlled by the function generator for each bias illumination intensity, and the record transient photovoltage decay signals were fitted using an exponential decay function for determining the decay time constants.

The GIWAXS measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu K $\alpha$  X-ray source (8.05 eV, 1.54 Å) and a Pilatus 3r 300 K detector. The incident angle was 0.2°.

For the transient photovoltage and transient photocurrent measurements, the device was serially connected to a digital oscilloscope (Tektronix TDS 3052C), and the input impedance of the oscilloscope was set to 1 M $\Omega$  and 50 M $\Omega$ , respectively, to form the open- and short-circuit conditions. The transient photovoltage was measured under 0.3 Sun illumination. An attenuated laser pulse (0.54 µJ cm-2; 530 nm) was used as a small perturbation to the background illumination. The transient photocurrent of the devices was measured by applying 530 nm laser pulses with a pulse width of 120 fs and a low pulse energy to the short-circuited devices in the dark.

*Calculation of bandgaps of polymers and acceptors:* The optical bandgap ( $E_g^{opt}$ ) can be calculated by the intersection of the linear fitting curve of the absorption edge and the abscissa axis (or the tangent of absorption tail). The photovoltaic bandgap ( $Eg^{PV}$ ) is the bandgap determined from the derivatives of the EQE<sup>PV</sup> spectra. The edge bandgap

(Eg<sup>edge</sup>) is given by the crossing point between the EQE<sup>PV</sup> spectra edge and the horizontal tangent of the EQE<sup>PV</sup> peak.

The voltage loss, determined by the difference between the optical gap  $(E_{g})$  and the open-circuit voltage  $(V_{oc})$ , is one of the most important parameters determining the performance of organic solar cells (OSCs). However, the variety of different methods used to determine  $E_g$  makes it hard to fairly compare voltages losses among different material systems. Eg determination for photoactive layers prepared under different condition using different methods were shown in Figure S4. The most commonly used method of determining the optical gap for voltage loss calculations is to take Eg, by the intersection of the linear fitting curve of the absorption spectrum and the abscissa axis (or the tangent of absorption tail). This approach is subjective and results are not well reproducible, especially when there is no strict linear region in the absorption edge or when the light scattering is very significant for the absorption tail, which is often the case for spin-coated organic films. In addition, using the absorption onset usually yields smaller values for  $E_g$  as compared with other determination methods, and hence leads to lower voltage losses. Furthermore,  $E_g^{PV}$  is the optical gap determined from the derivatives of the EQE<sup>PV</sup> spectra.  $E_g^{PV}$  represents an external property of a photovoltaic device and not an (internal) property of a photovoltaic material as, e.g., the Tauc gap (Tauc, Mater. Res. Bull. 1968, 1,37). We note that a definition of the band gap similar to our proposition was given earlier by Aiken et al. (D. Aiken et al. Piscataway, New Jersey, 2002, p. 828.). The external definition via a distribution of SQ-type band-gap energies as proposed here aims at a consistent analysis of losses for a solar cell entirely

from its external properties.  $E_g^{edge}$  is given by the crossing point between the  $EQE^{PV}$ spectra edge and the horizontal tangent of the  $EQE^{PV}$  peak.



Fig. S1. AFM images of pure (a) PBDF-BDD and (b) IT-4F with different amounts of

DIO or DPE.



Fig. S2. AFM images of PBDF-BDD: IT-4F based blend films with different amounts of (a) DIO or (b) DPE.



**Fig. S3.** The corresponding in-plane (red lines) line and out-of-plane (black lines) cuts of (a) PBDF-BDD, (b) IT-4F.



**Fig. S4.** The dependence of photocurrent density  $(J_{ph})$  and SCLC characteristics of the PBDF-BDD: IT-4F based devices with different concentration of DIO and DPE.





**Fig. S5**. Eg determination for photoactive layers prepared under different condition using different methods. (a-e) PBDF-BDD: IT-4F with different concentration of DPE, (f-i) and DIO. Eg<sup>PV</sup> is the optical gap determined from the derivatives of the EQE spectra and edge Eg is given by the crossing point between the EQE spectra edge and horizontal tangent of EQE peak.





Fig. S6. sEQE and normalized electroluminescence spectra of (a-c) PBDF-BDD: IT-

4F with different concentration of DPE, (d-f) and DIO.



**Fig. S7.** Transient photovoltage (TPV) decay kinetics of devices with different additives as a function of bias light intensity of 1 sun.



Fig. S8. The GPC distribution plot of PBDF-BDD.

Solvent	Formula (M.W.)	Boiling point (°C)	Vapor pressure (Pa, at 25 ºC)	Ref.
DIO	C8H16I2 (366.02)	363-366	0.0375	1
DBrO	C8H16Br2 (272.02)	270-272	0.53 (20.6 °C) 1.34 (30.6 °C)	2
CN	C10H7Cl (162.62)	260-263	3.87-4.00	3
DPE	C12H10O (170.21)	258-260	2.70-3.00	4
CF	CHCl3 (119.38)	60.5-61.5	26264.5	5

 Table S2. The roughness of PBDF-BDD: IT-4F with different concentration of DIO

 and DPE.

additiva	Ratio	RMS
auuntive	(%)	(nm)
	0.5	2.53
DIO	1	3.48
DIO	3	3.95
	5	6.21
	0.5	2.61
DDE	1	3.78
DFE	3	3.34
	5	3.85
W/O	0	2.38

 Table S3. The mobility data of OSCs

SA	Ratio (%)	μ <sub>h</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	μ <sub>e</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_{h}/\mu_{e}$
	0.5	2.12×10 <sup>-4</sup>	1.05×10 <sup>-4</sup>	2.02
DIO	1	2.10×10 <sup>-4</sup>	1.00×10 <sup>-4</sup>	2.10
DIO	3	2.25×10 <sup>-4</sup>	0.95×10 <sup>-4</sup>	2.37
	5	2.50×10 <sup>-4</sup>	1.00×10 <sup>-4</sup>	2.5
	0.5	1.48×10 <sup>-4</sup>	0.62×10 <sup>-4</sup>	2.39
DDE	1	1.60×10 <sup>-4</sup>	0.65×10 <sup>-4</sup>	2.46
DFE	3	2.00×10-4	0.65×10-4	3.08
	5	2.15×10-4	0.70×10 <sup>-4</sup>	3.07
W/O		1.62×10 <sup>-4</sup>	0.52×10-4	3.10

Table S4. The  $\text{EQE}_{\text{EL}}$  value of devices with different additives.

SA	Ratio (%)	qV <sup>SQ</sup> (eV)	EQE <sub>EL</sub>
	0.5	1.307	2.81×10-6
DIO	1	1.288	4.04×10 <sup>-6</sup>
DIO	3	1.288	1.04×10 <sup>-5</sup>
	5	1.288	2.42×10 <sup>-6</sup>
	0.5	1.324	2.73×10 <sup>-5</sup>
DPE	1	1.324	1.65×10-5
	3	1.324	1.69×10 <sup>-5</sup>

	5	1.324	2.14×10 <sup>-5</sup>
w/o		1.324	2.18×10-5

 Table S5. The roughness of PBDF-BDD: IT-4F with different concentration of DIO and DPE.

additive	Ratio	RMS
	(%)	(nm)
W/O	0	0.388
DIO	0.5	0.414
	5	1.070
DPE	0.5	0.377
	5	0.494
W/O	0	0.888
DIO	0.5	1.020
210	5	5.980
DPE	0.5	1.080
	5	3.420
ad IT-4F		additive         Ratio (%)           W/O         0           DIO         0.5           DPE         0.5           W/O         0           DIO         0.5           DPE         0.5           W/O         0           DIO         0.5           S         0           DIO         0.5           S         0           DIO         0.5           S         5           DPE         0.5           5         5           DPE         0.5           5         5           DPE         5

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