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## Regulating the morphology of fluorinated non-fullerene acceptor and polymer donor via binary solvent mixture for high efficiency polymer solar cells

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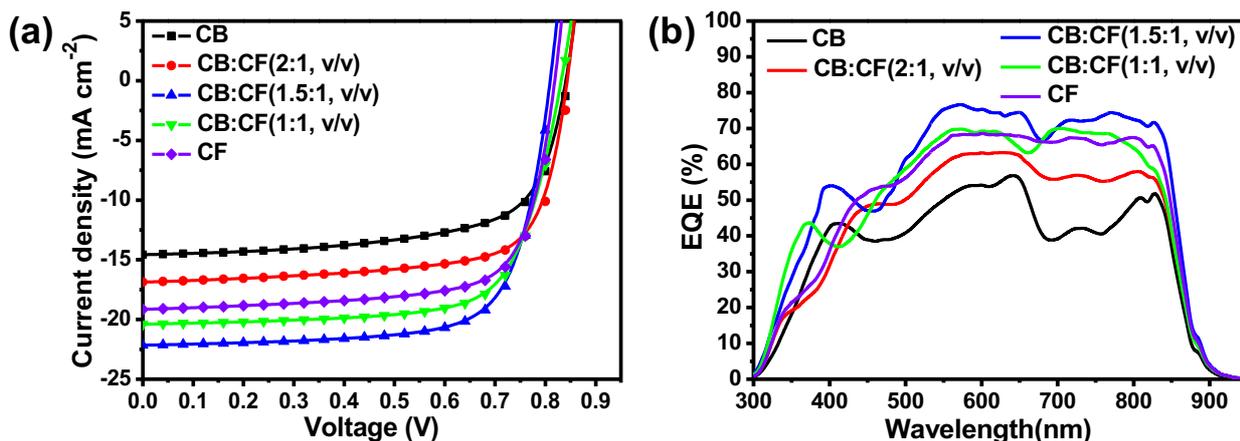
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**Table S1** Summary of photovoltaic parameters of PBDB-T:INPIC-4F OSCs processed using binary solvent mixtures (CB:CF=1.5:1, v/v) and different treatments.

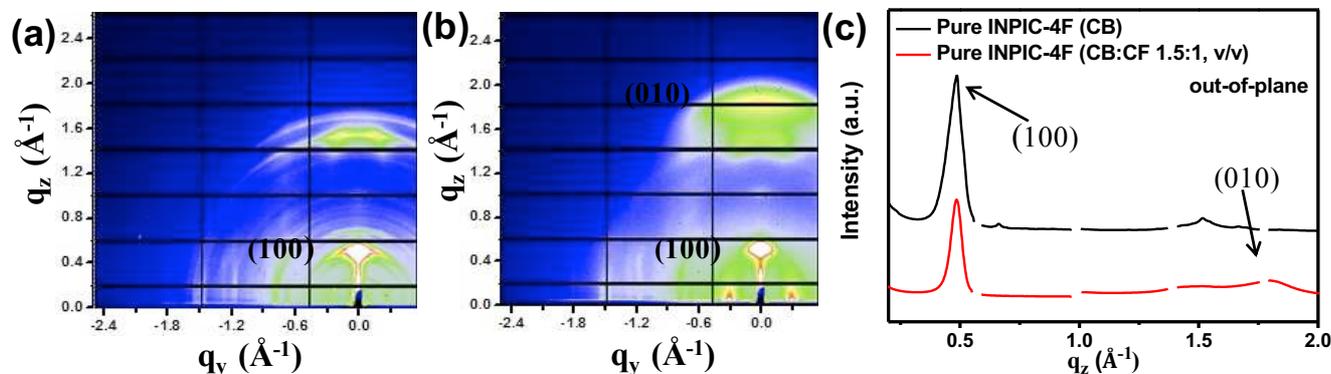
Treatment	$FF$ [%]	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	$PCE_{max}(PCE_{avg})$ [%]
0.5%DIO+100 °C TA	72.7	22.0	0.82	13.1 (12.9 ± 0.3)
0.5%DIO only	70.9	19.9	0.85	12.0 (11.7 ± 0.4)
100 °C TA only	68.4	20.3	0.84	11.7 (11.3 ± 0.4)
—	67.2	18.8	0.85	10.8(10.3 ± 0.6)



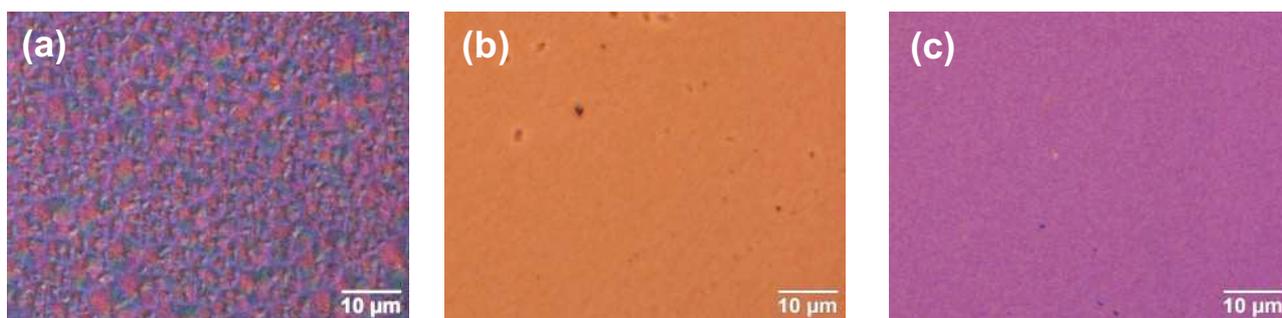
**Figure S1** (a)  $J$ - $V$  characteristics of the PBDB-T:INPIC-4F (1:1, w/w) devices under illumination of AM 1.5G ( $100\text{mW cm}^{-2}$ ). (b)  $EQE$  of devices fabricated under different processing conditions.

**Table S2** Summary of photovoltaic parameters of PBDB-T:INPIC-4F OSCs with different casting solvents measured at an illumination of AM 1.5G at  $100\text{ mW cm}^{-2}$ . The statistical data were obtained from over 25 individual devices.

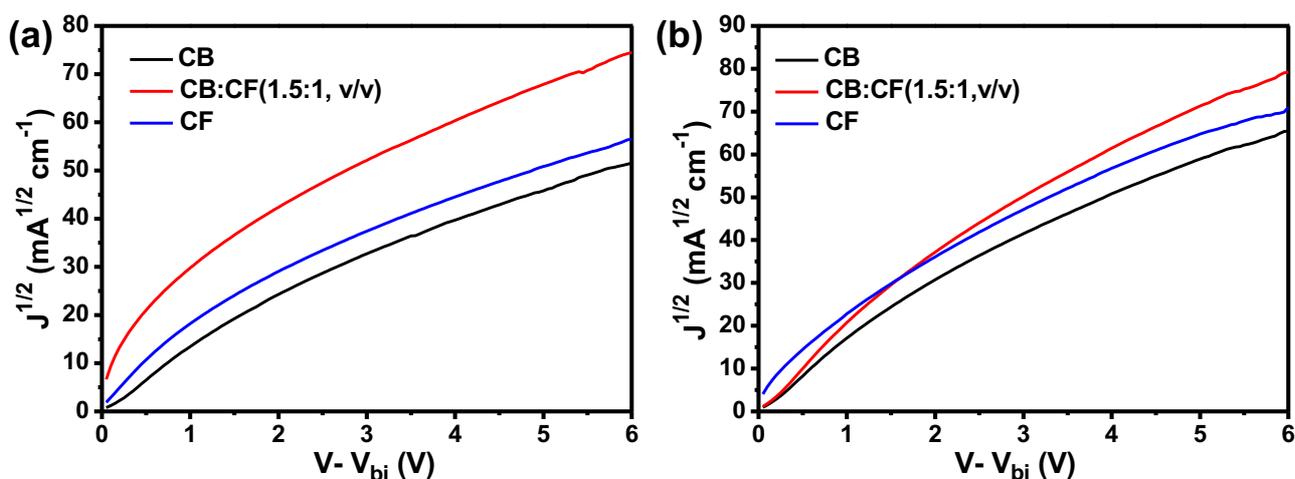
Solvent	$FF$	$J_{sc}$	Calculated $J_{sc}$	$V_{oc}$	$PCE_{max}$ ( $PCE_{avg}$ )
	[%]	[ $\text{mA cm}^{-2}$ ]	[ $\text{mA cm}^{-2}$ ]	[V]	[%]
CB	66.5	14.6	14.0	0.84	8.1 ( $7.4 \pm 0.9$ )
CB:CF(2:1, v/v)	71.5	16.9	16.2	0.84	10.2 ( $9.7 \pm 0.7$ )
CB:CF(1.5:1, v/v)	72.7	22.0	21.4	0.82	13.1 ( $12.9 \pm 0.3$ )
CB:CF(1:1, v/v)	71.6	20.4	19.8	0.83	12.1 ( $11.8 \pm 0.4$ )
CF	72.2	19.1	18.5	0.83	11.4 ( $11.0 \pm 0.5$ )



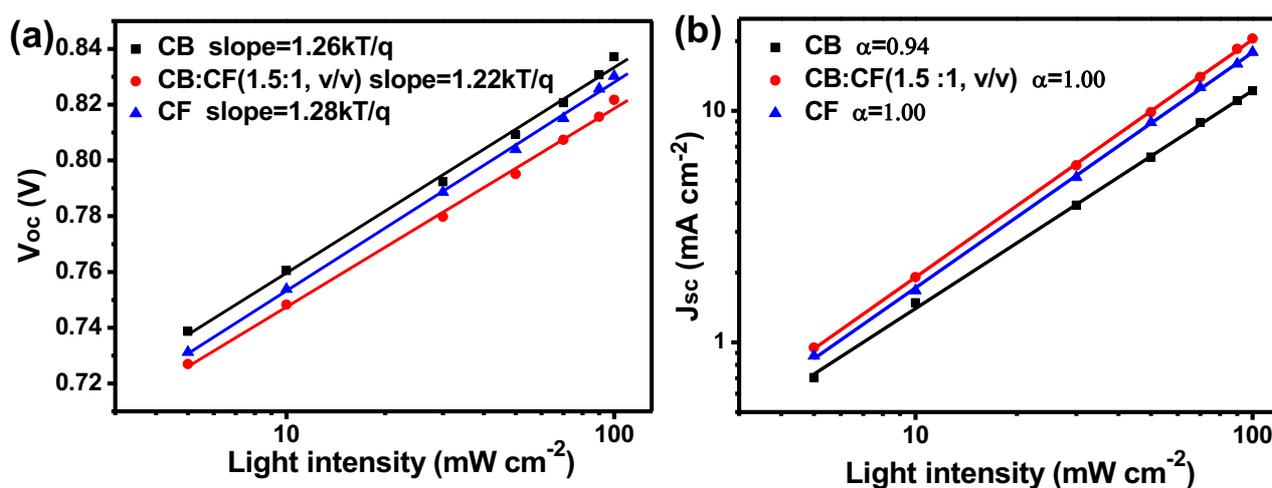
**Figure S2** 2D GIWAXS patterns of pristine INPIC-4F films prepared from (a) CB, (b) CB:CF (1.5:1, v/v). (c) Out-of-plane 1D profiles of GIWAXS patterns along the  $q_z$  axis.



**Figure S3** Optical microscope images of PBDB-T: INPIC-4F films prepared from (a) CB, (b) CB:CF (1.5:1, v/v) and (c) CF.



**Figure S4** Root square plots of (a) hole densities versus voltage of the ITO/PEDOT:PSS/Active layer/MoO<sub>3</sub>/Ag hole-only devices and (b) electron densities versus voltage of the ITO/TiO<sub>2</sub>/Active layer/Ca/Ag electron-only devices. The linear fit was applied in the range of 0 to 6 V.



**Figure S5** (a)  $V_{oc}$  versus light intensity and (b)  $J_{sc}$  versus light intensity of PBDB-T:INPIC-4F OSCs cast from various solvents.