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Electronic Supplementary Information

Molecular Ordering and Phase Segregation Induced by a Volatile Solid Additive for Highly Efficient All-Small-Molecular Organic Solar Cells

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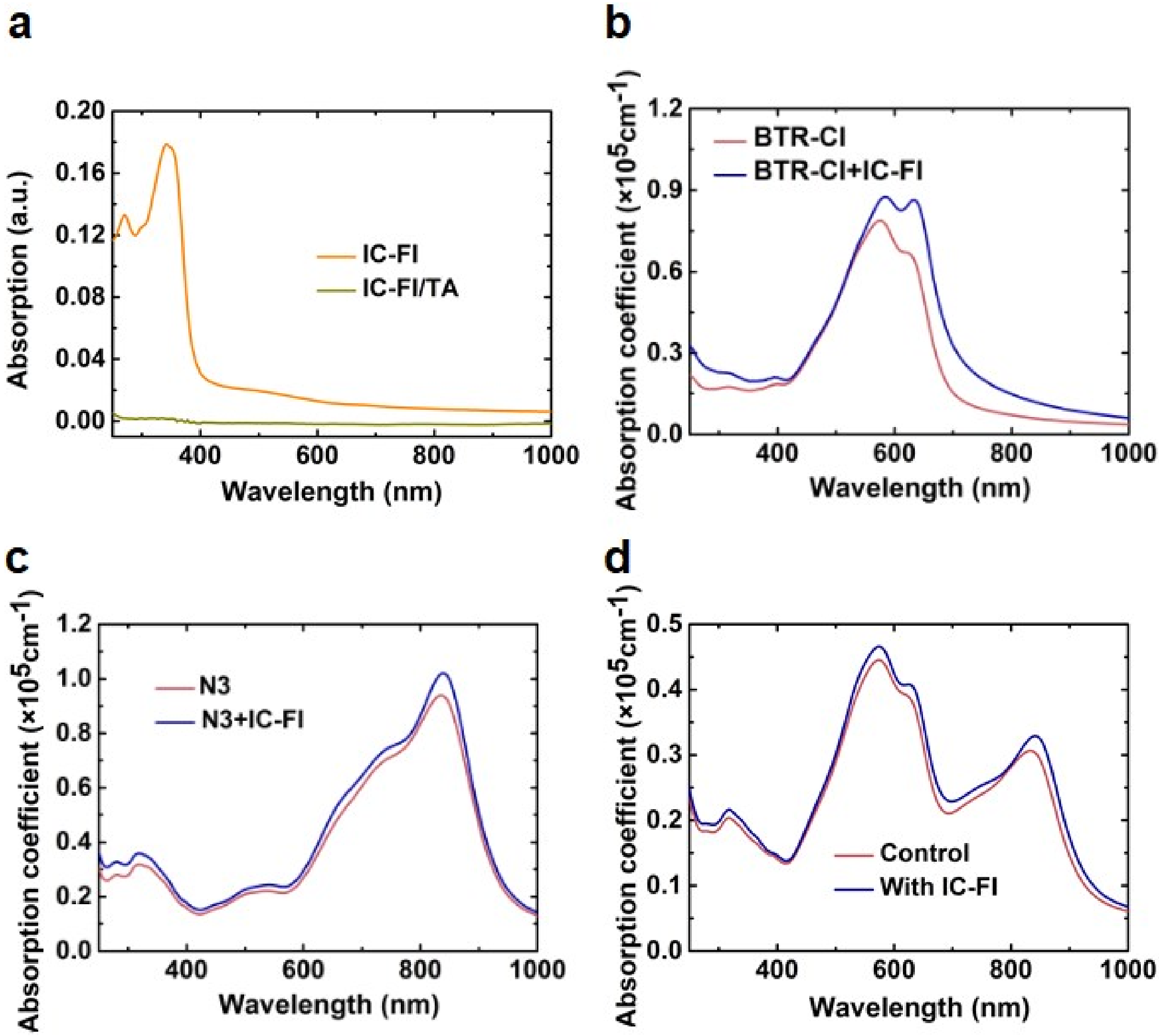

Fig. S1 (a) The absorption spectra of IC-FI film before and after 120 ^{o}C annealing for 5 min. The absorption coefficient spectra of (b) BTR-Cl/TA and IC-FI-processed BTR-Cl films, (c) N3/TA and IC-FI-processed N3 films, (d) BTR-Cl:N3/TA and IC-FI-processed BTR-Cl:N3 blend films.

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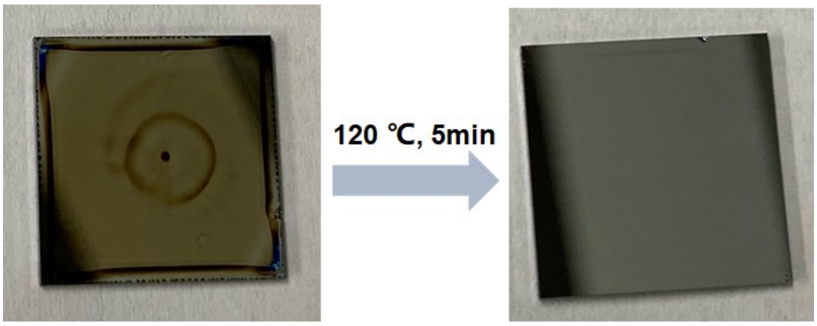

Fig. S2 The images of the IC-FI film coated on the Si substrate before and after 120 °C annealing for 5 min.

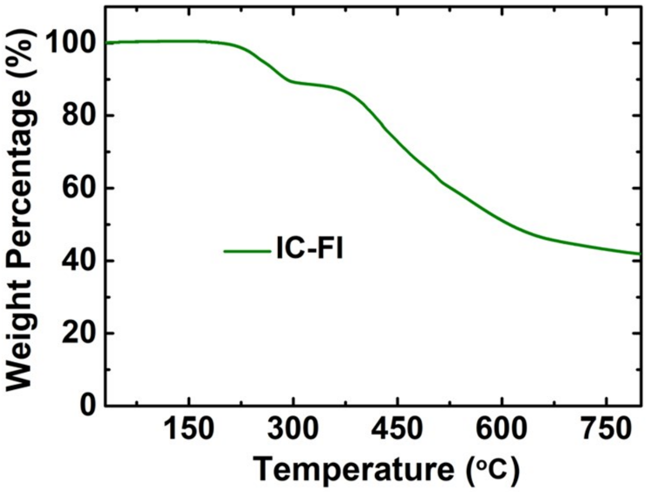

Fig. S3 The TGA plot of IC-FI at a scan rate of 10 °C/min.

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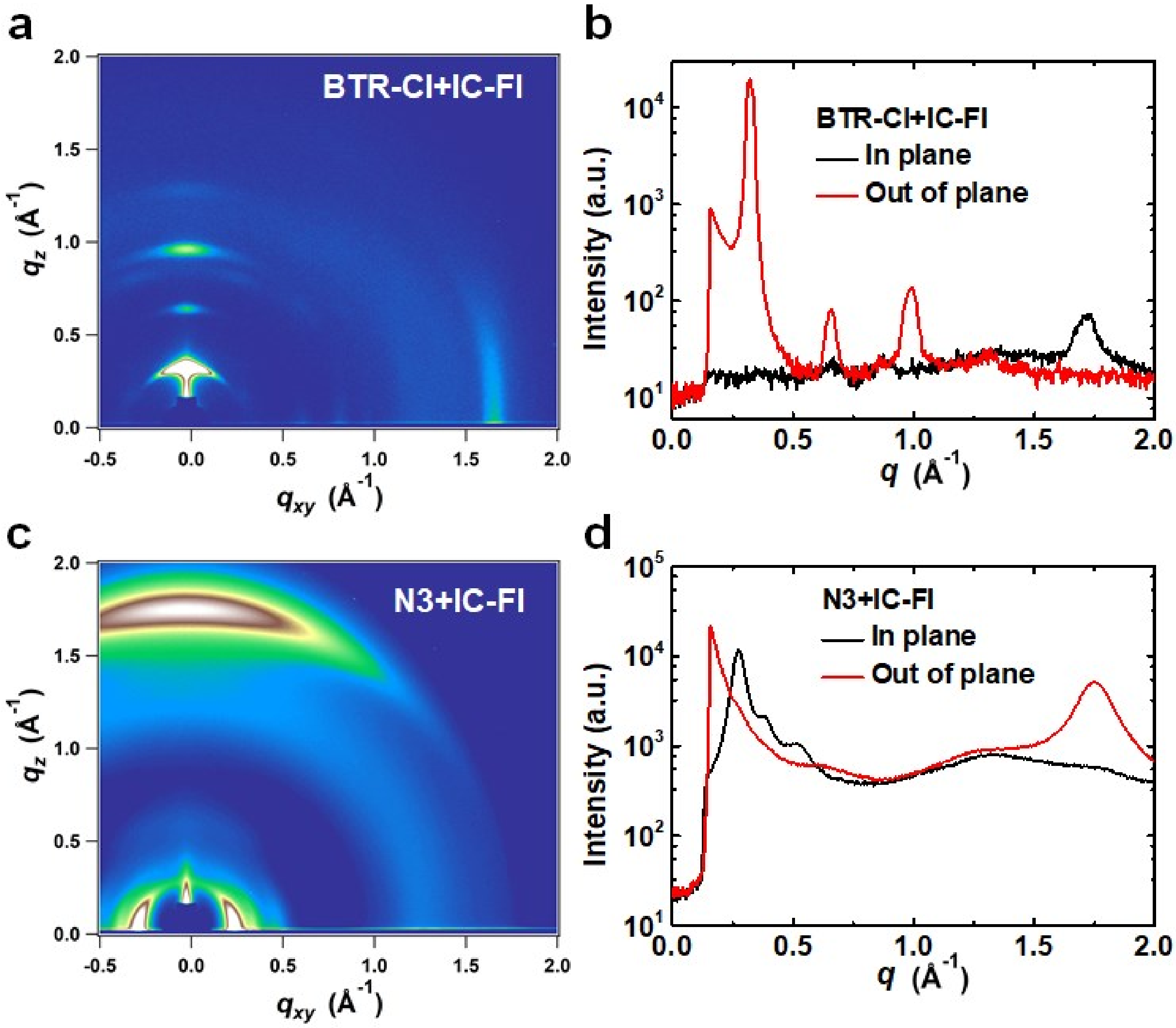

Fig. S4 (a) GIWAXS patterns of BTR-Cl+IC-FI film, and (b) the corresponding in-plane and out-of-plane line cuts. (c) GIWAXS patterns of N3+IC-FI films, and (d) the corresponding in-plane and out-of-plane line cuts.

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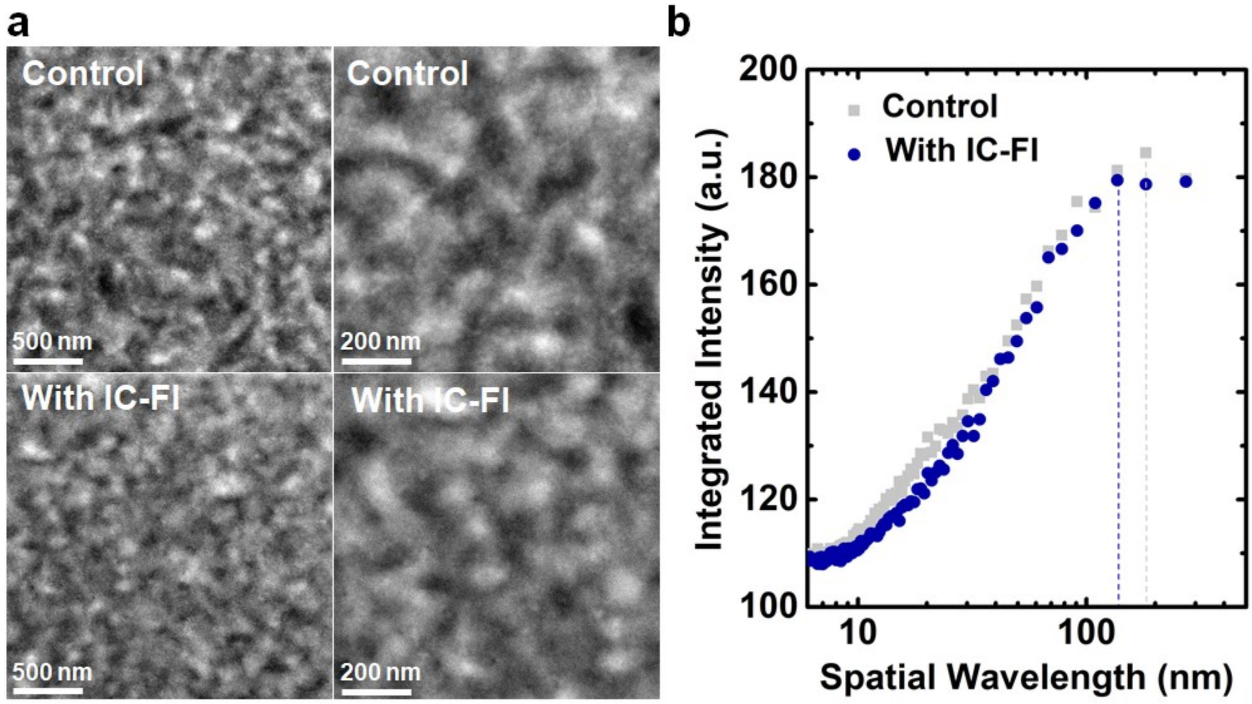

Fig. S5 (a) The HAADF-STEM images of control and IC-FI-processed blend films under different magnification. (b) The corresponding radially averaged two-dimensional discrete Fourier transform.

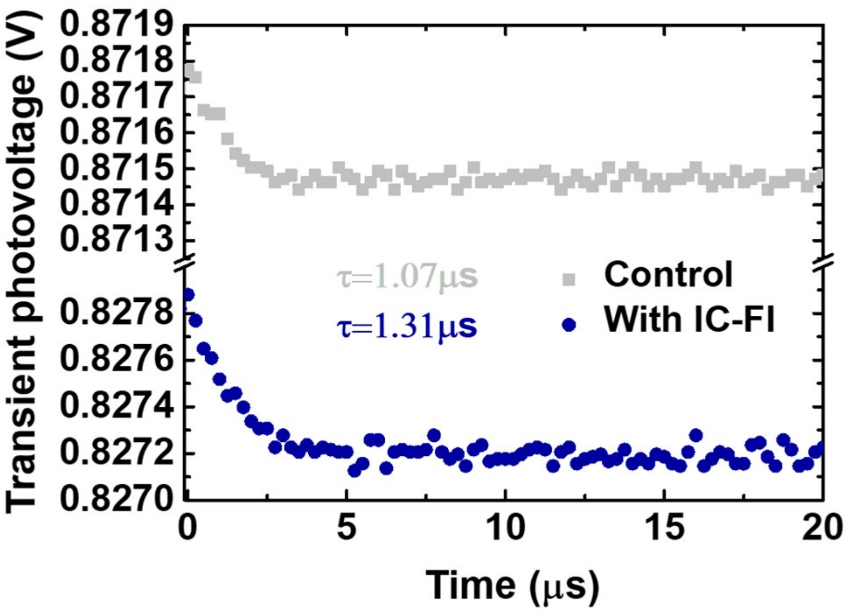

Fig. S6 TPV properties in devices at one sun condition.

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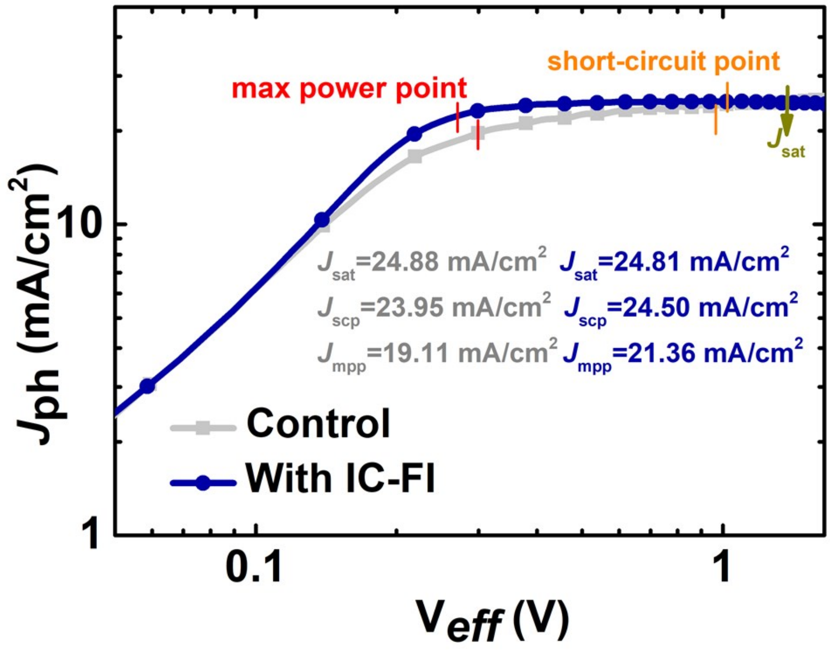

Fig. S7 The net photocurrent (J_{ph}) versus effective voltage (V_{eff}) characteristics in the control and IC-FI-processed devices.

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Table S1. GIWAXS characteristics of the neat and blend films.

Crystallographic Parameter			Neat Films		Blend Films	
			BTR-Cl	N3	Control	With IC-FI
π-π stack (010)	In-plane	q_{xy} (Å^{-1})	1.710	-	1.731	1.749
		d-spacing (Å)	3.675	-	3.629	3.592
		FWHM (Å^{-1})	0.087	-	0.156	0.177
		CCL[a)] (nm)	6.553	-	3.675	3.237
		CCL[b)] (nm)	6.478	-	3.631	3.198
	Out-of-plane	q_z (Å^{-1})	-	1.743	1.703	1.720
		d-spacing (Å)	-	3.605	3.689	3.654
		FWHM (Å^{-1})	-	0.171	0.203	0.135
		CCL[a)] (nm)	-	3.341	2.814	4.234
		CCL[b)] (nm)	-	3.302	2.782	4.190

[a)] The CCL values were calculated via $\mathrm{CCL} = \dfrac{K\lambda}{(2\sin^{-1}(\frac{\lambda\Delta q}{4\pi})) \times \cos(\sin^{-1}(\frac{q\lambda}{4\pi}))}$, where K is a numerical factor frequently referred to as the crystallite-shape factor (0.9), λ is the wavelength of the X-rays (1.10994 Å), q is the magnitude of the scattering vector, and Δq is the corresponding FWHM.[1-2]

[b)] The CCL values were calculated via CCL=2πK/Δq equation, where the K value is 0.9, and Δq is the FWHM.[3]

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Table S2. Photovoltaic parameters for the BTR-Cl:N3 based devices processed with different amounts of IC-FI respect to the N3 acceptor.

Condition	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
0 wt%	0.85	24.16	64.7	13.36
24 wt%	0.81	23.41	68.3	12.99
30 wt%	0.81	24.71	70.4	14.12
36 wt%	0.82	24.06	73.5	14.43
42 wt%	0.80	24.39	71.3	13.90
48 wt%	0.80	23.47	70.1	13.29

Table S3. Photovoltaic parameters for the BTR-Cl:N3 based devices processed with 36 wt% IC-FI under different annealing temperatures.

Condition	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
80 ^{o}C, 5 min	0.46	22.60	45.7	4.75
100 ^{o}C, 5 min	0.66	24.14	56.8	9.10
120 ^{o}C, 5 min	0.82	24.06	73.5	14.43
140 ^{o}C, 5 min	0.81	23.12	71.2	13.36
160 ^{o}C, 5 min	0.79	21.56	69.0	11.81

Table S4. Photovoltaic parameters for the BTR-Cl:N3 based devices processed with 36 wt% IC-FI under different annealing time.

Condition	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
120 ^{o}C, 0 min	0.44	6.32	27.9	0.77
120 ^{o}C, 5 min	0.82	24.06	73.5	14.43
120 ^{o}C, 10 min	0.83	23.94	72.3	14.37
120 ^{o}C, 20 min	0.82	23.68	71.9	13.97

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Table S5. Summary of the representative ASM OSCs works reported in recent five years.

Active Layer	Treatment Method	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	Reference
DRCN5T: $PC_{71}BM$	TA+SVA	0.92	15.88	69.0	10.1	*J. Am. Chem. Soc.* **2015**, *137*, 3886
BTID-2F: $PC_{71}BM$	None	0.95	15.7	76.0	11.3	*Nat. Commun.* **2016**, *7*, 13740
SM1:IDIC	TA	0.91	15.18	73.5	10.1	*Chem. Mater.* **2017**, *29*, 7543
NDT-3T-R6: IDIC-4F	TA	0.78	18.89	72.8	10.7	*Adv. Energy Mater.* **2018**, 1803175
ZnP-TBO: 6TIC	DIO+SVA	0.80	20.44	73.87	12.08	*Adv. Mater.* **2019**, 1807842
BTR-Cl:Y6	TA	0.86	24.17	65.5	13.6	*Joule* **2019**, *9*, 009
ZR1:Y6	TA	0.86	24.34	68.44	14.3	*Nat. Commun.* **2019**, *10*, 5393
BTR-Cl:Y6	0.3%DIO+TA	0.83	23.66	74.7	14.7	*Adv. Energy Mater.* **2020**, 2001076
B1:BO-4Cl	SVA	0.83	25.27	73.0	15.3	*Sci. China Mater.* **2020**, *63*, 1142
BTR-Cl:N3	**36.0 wt% IC-FI (solid)+TA**	**0.82**	**24.06**	**73.53**	**14.43**	**This work**

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