Supplementary Information

A Low Boiling-Point and Low-cost Fluorinated Additive Improves the Efficiency and Stability of Organic Solar Cells

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Experimental Section

Materials: All chemicals and solvents were purchased from J&K, Alfa Aesar and TCI Chemical Co. J71 was purchased from Solarmer Materials, Inc. PDINO were obtained according to our previous reported methods. *m*-ITTC was prepared according to the procedure reported in literature.

Fabrication of PSCs: The PSCs were fabricated with traditional device structure of ITO /PEDOT: PSS/J71:*m*-ITTC/PDINO/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, and isopropanol for 15 min respectively. After dried under a nitrogen stream, and subsequent ultraviolet-ozone treatment for 30 min, a thin layer of PEDOT: PSS was prepared on precleaned ITO glass through spin-coating a PEDOT: PSS aqueous solution (Baytron P VP AI 4083 from H. C. Starck) at 4200 rpm and dried subsequently at 150 ℃ for 20 min in air. Then the PEDOT:PSS coated ITO substrate was transferred to a nitrogen glove box, where the active blend layer of J71:*m*-ITTC was spin-coated from its chloroform solution with or without DFB additive onto the PEDOT: PSS layer at 4200 rpm. After spin-coating, the active layers were annealed at 150 ℃ for 2 min for the devices with TA treatment. The electron transport layer PDINO was spin-coated from its solution at a concentration of 1.0 mg mL^{-1}. Finally, cathode metal Al was deposited at a pressure of 5.0×10^{-5} Pa. The active layer effective area of the devices was 4.6 mm^2.

Characterization of the OSCs: The current density-voltage (*J-V*) characteristics of the OSCs were measured on a computer-controlled Keithley 2450 Source-Measure Unit, under AM 1.5G solar illumination at 100 mW cm^{-2} using a Newport solar simulator. EQE spectra were measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan).

Measurements: The UV-visible absorption spectra were measured on a Hitachi U-3010 UV-vis spectrophotometer. The thickness of the thin films was measured by a profilometry (Ambios Tech.XP-2). The surface morphology of thin films was measured by atomic force microscope (AFM, Bruker-ICON2-SYS) in the tapping mode. The bulk morphology of thin films was measured by transmission electron microscopy (TEM, JEM-2100F).

SCLC Measurements: Hole and electron mobilities were measured using the SCLC model. ITO/PEDOT: PSS/active layer/Au for hole-only devices and ZnO/ active layer /PDINO/Al for electron-only devices. The SCLC mobilities were calculated by Mott–Gurney equation: = (9/8) $\varepsilon_r\varepsilon_0\mu(V^2/L^3)$ where J is the current density, ε_r is the dielectric permittivity of the active layer, ε_0 is the vacuum permittivity, L is the thickness of the active layer, μ is the mobility. $V=V_{app}$ - V_{bi}, where V_{app} is the applied voltage, V_{bi} is the offset voltage (V_{bi} is 0 V here). The mobility can be calculated from the slope of the $J^{0.5}\sim V$ curves.

GIWAXS Characterization: The samples for the GIWAXS measurements were prepared on Si substrates using chloroform solutions of the samples.

Table S1. Photovoltaic performance parameters of the OSCs based on J71: *m*-ITTC with different D/A ratio.

Devices	Blend ratio	condition	*Voc* (V)	*Jsc* (mA cm^{-2})	*FF* (%)	PCE_{max} (PCE_{avg}[a])[%]
J71:*m*-ITTC	1:1	TA130°C,2min	0.88(±0.007)	17.16(±0.19)	66.53(±1.36)	10.10(9.85)
	1:1.2	TA150°C,2min	0.87(±0.009)	17.42(±0.21)	72.81(±1.46)	11.01(10.81)
	1:1.5	TA130°C,2min	0.88(±0.007)	16.78(±0.05)	69.57(±1.55)	10.29(9.99)
	1.2:1	TA150°C,2min	0.88(±0.004)	18.06(±0.08)	63.53(±1.64)	10.11(9.87)
	1.5:1	TA130°C,2min	0.88(±0.005)	17.20(±0.08)	55.04(±1.19)	8.37(8.03)

a) Average PCE from 20 devices.

Table S2. Photovoltaic performance parameters of the OSCs based on J71: *m*-ITTC with different additives ratio.

Devices	Additive ratio(v/v)	condition	*Voc* (V)	*Jsc* (mA cm−2)	*FF* (%)	PCE_{max} (PCE_{avg}[a])[%]
J71:*m*-ITTC	0.4%	150°C,2min	0.88(±0.006)	18.02(±0.12)	70.66(±0.62)	11.13(11.02)
	0.8%	150°C,2min	0.87(±0.009)	19.27(±0.17)	73.54(±0.64)	12.38(12.04)
	1.2%	150°C,2min	0.88(±0.006)	17.49(±0.38)	70.07(±0.44)	10.88(10.66)

(a) Average PCE from 20 devices.

Table S3. Charge Transport Properties of the J71:*m*-ITTC Blend Films

Active layer	1,4-difluorobenzene (%, v/v)	Thickness (nm)	μ_e (10^{-5}cm^{2}v^{-1}s^{-1})	μ_h (10^{-4}cm^{2}v^{-1}s^{-1})	μ_h/μ_e
J71:*m*-ITTC	As cast	150	2.60	7.30	0.03
	0.4	150	4.43	4.77	0.09
	0.8	150	4.37	8.83	0.05
	1.2	150	4.12	7.40	0.05

Table S4. Comparison of the prices of the currently used additive.

Name	Selling price[(a)]
1,8-Diiodooctane (DIO)[1-4] ,97+%	74.6 RMB/g
1-Chloronaphthalene (CN)[5, 6], 97.0%	63.6 RMB/g
1,8-Octanedithiol (ODT)[7, 8], 99%	398.5 RMB/g
1-Phenylnaphthalene (PN)[9],97%	119.6 RMB/g
Diphenyl ether (DPE)[10],99%	76.75 RMB/g
N-Methylpyrrolidone (NMP)[11]	13392 RMB/g
1,4-Difluorobenzene (DFB) 99% this work	4.05 RMB/g

(a) Since there may be certain differences in the prices of different purchasing companies, our additives are purchased from J&K, so we choose to use the selling price on J&K as the standard for comparison.

Table S5. Photovoltaic performance parameters of the OSCs based on J71: *m*-ITTC

(1:1.2, w/w) with 150 ℃ TA treatment (with 0.8% v/v or without additive) under the illumination of AM1.5G, 100 mW/cm^2.

DFB[v%]	TA(Time)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE_{max} (PCE_{avg}[a]) [%]
without	5min	0.87(±0.001)	17.60(±0.005)	70.21(±0.14)	10.75(10.60)
	10min	0.87(±0.001)	17.65(±0.02)	68.84(±0.05)	10.58(10.44)
	20min	0.87(±0.001)	17.52(±0.01)	66.24(±0.10)	10.12(9.95)
	30min	0.86(±0.001)	17.35(±0.01)	60.38(±0.35)	9.01(8.90)
0.8%	5min	0.87(±0.001)	18.10(±0.06)	70.13(±0.32)	11.08(10.83)
	10min	0.87(±0.001)	17.75(±0.02)	70.28(±0.08)	10.89(10.69)
	20min	0.87(±0.002)	17.71(±0.04)	68.07(±0.56)	10.45(10.31)
	30min	0.87(±0.003)	17.69(±0.03)	67.07(±0.37)	10.34(10.20)

(a) Average PCE from 20 devices.

Table S6. Photovoltaic performance parameters of the OSCs based on J71: *m*-ITTC with DIO or CN additive treatment under the illumination of AM 1.5G, 100 mW cm^{-2}.

Devices	Additive ratio(v/v)	condition	Voc (V)	Jsc (mA cm−2)	FF (%)	PCE_{max} (PCE_{avg}[a])[%]
J71:*m*-ITTC	0.8%CN	150℃,2min	0.92(±0.001)	17.34(±0.01)	68.44(±1.11)	10.91(10.58)
	0.8%DIO	150℃,2min	0.90(±0.001)	11.92(±0.06)	62.36(±0.23)	6.69(6.67)

(a) Average PCE from 10 devices.

Table S7. Photovoltaic performance parameters of the OSCs based on PTQ10:*m*-ITTC (1:1.2, w/w) with 150 ℃ 2 min TA treatment (with 0.8% v/v or without additive) under the illumination of AM1.5G, 100 mW/cm^2.

Devices	DFB [%]	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE_{max} (PCE_{avg}[a])[%]
PTQ10: *m*-ITTC	without	0.98(±0.001)	15.56(±0.01)	66.81(±0.53)	10.18(10.03)
	0.8%	0.98(±0.001)	15.72(±0.02)	66.95(±0.61)	10.31(10.27)

(a) Average PCE from 10 devices.

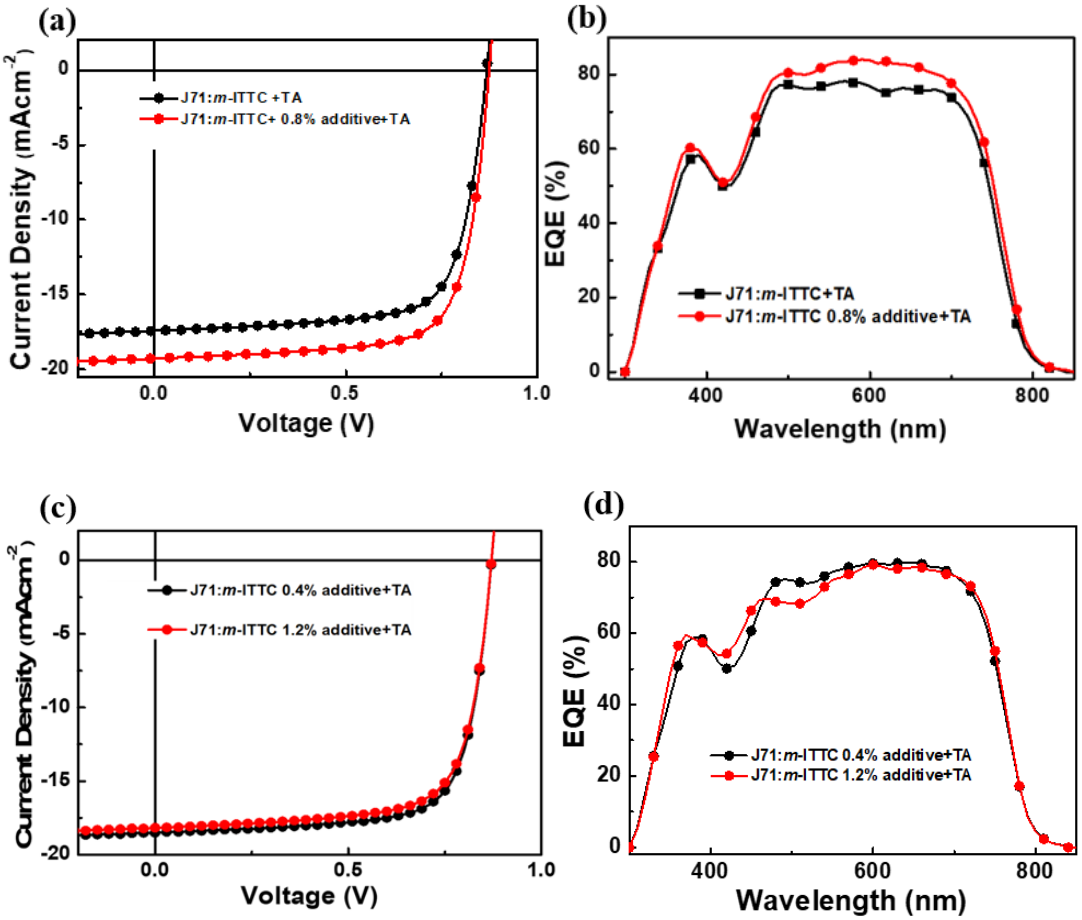

Figure S1. (a)(c) The *J-V* curves of devices based on J71:*m*-ITTC with different additive concentrations under the illumination of AM 1.5G, 100 mW cm^{-2}. (b)(d) EQE spectra of devices based on J71:*m*-ITTC with different additive concentrations.

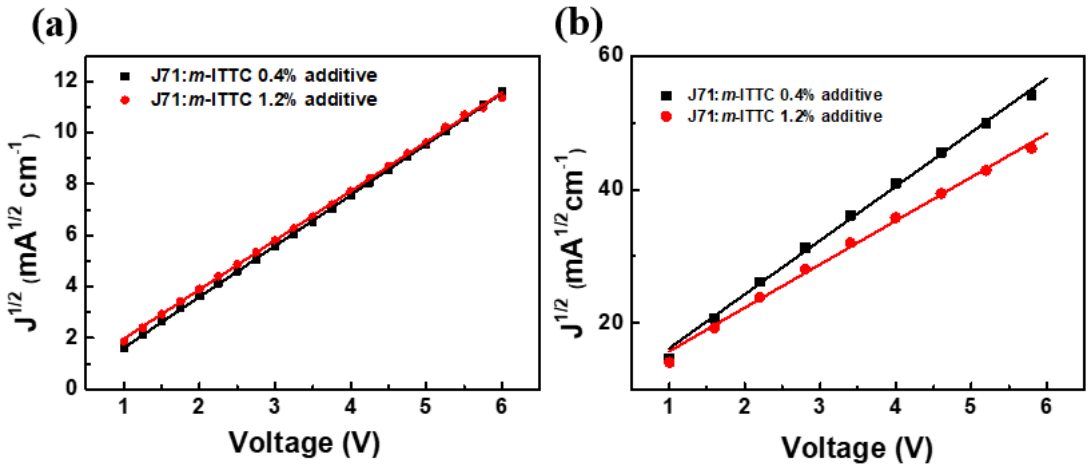

Figure S2. (a) *J-V* characteristics in the dark for the electron-only devices based on blend J71:*m*-ITTC films with different additive concentrations. (Electron mobility). (b) J-V characteristics in the dark for the hole-only devices based on blend J71: *m*-ITTC films with different additive concentrations. (Hole mobility).

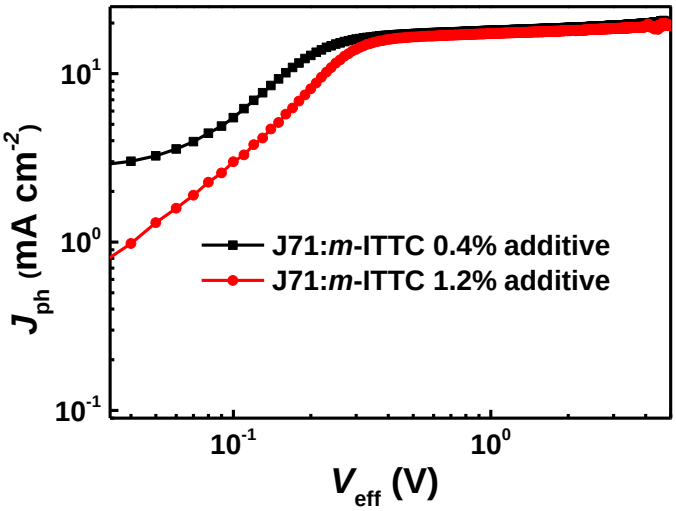

Figure S3. J_{ph} versus V_{eff} of the J71:*m*-ITTC devices with different additive concentrations.

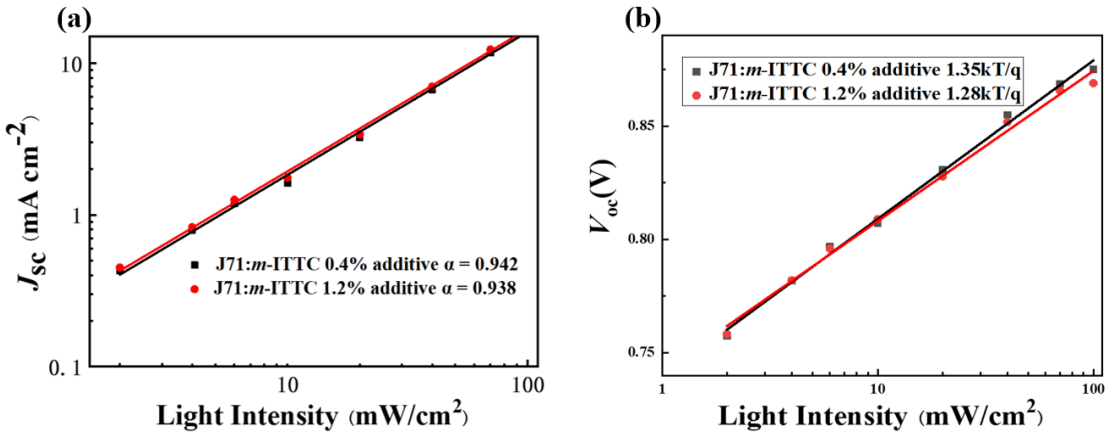

Figure S4. (a)Light intensity dependence of J_{sc} of the devices based on J71: *m*-ITTC blend films with different additive concentrations. (b) Light intensity dependence of V_{oc} of the devices based on J71: *m*-ITTC blend films with different additive concentrations.

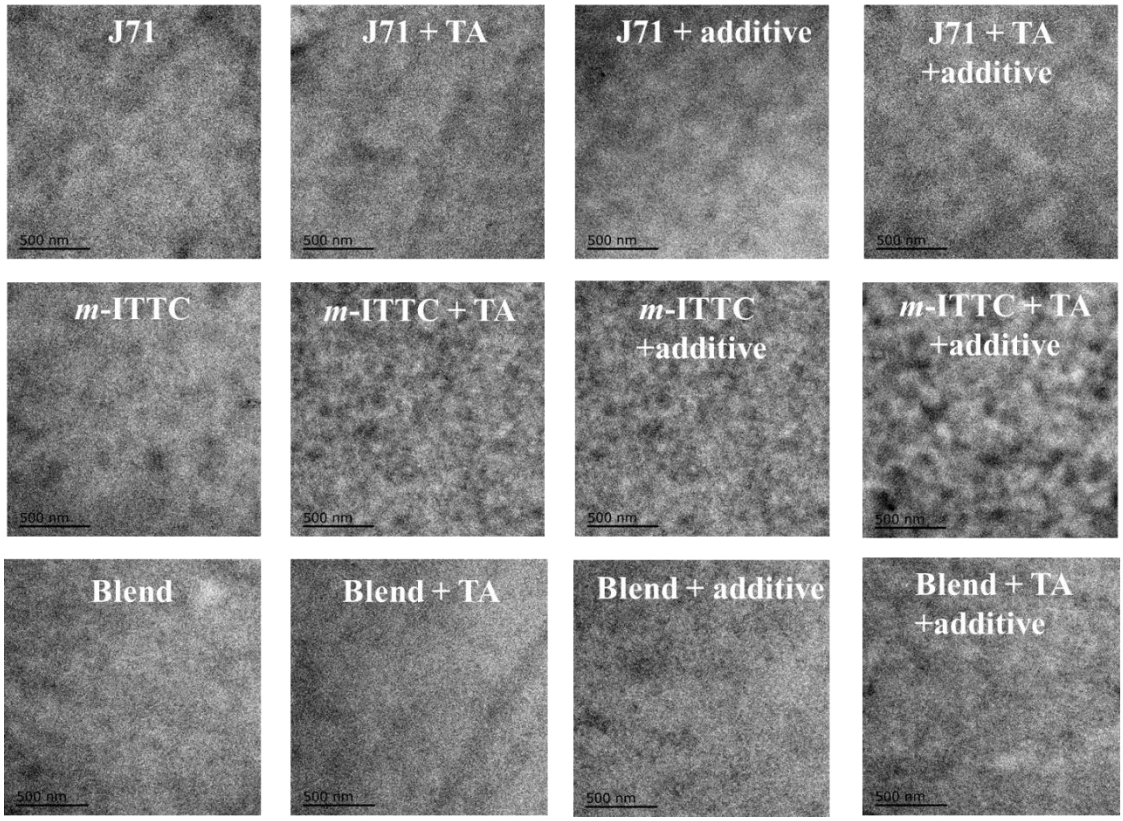

Figure S5. TEM images (scale bar = 500 nm) of different films.

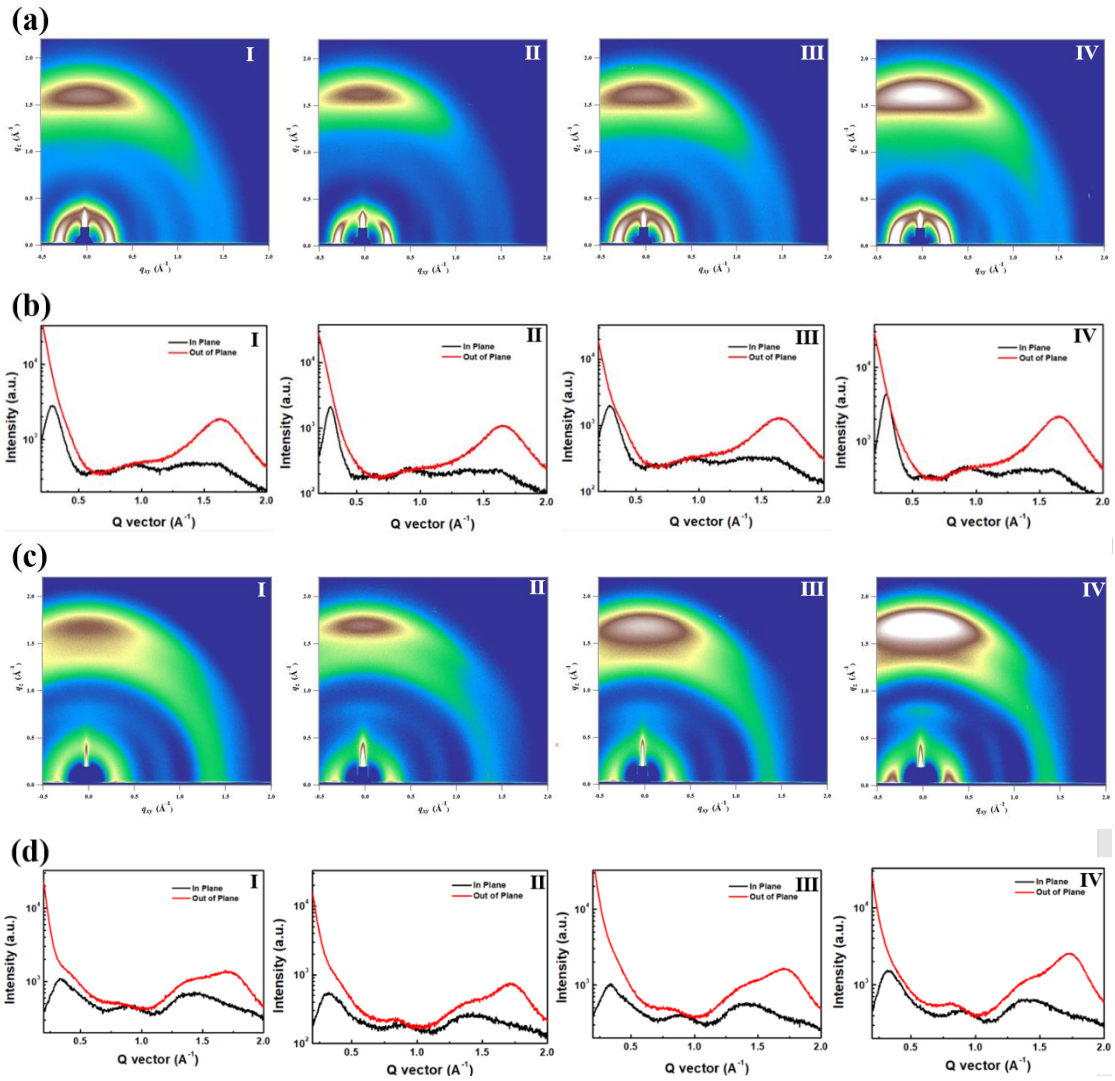

Figure S6. (a) GIWAXS patterns of the neat J71 film: (I) J71 as-cast, (II) J71 with TA treatment, (III) J71 with additive treatment, (IV) J71 with additive and TA treatment. (b) Corresponding line-cut profiles of the GIWAXS patterns of the neat J71 film. (c) GIWAXS patterns of the neat *m*-ITTC film: (I) *m*-ITTC as-cast, (II) *m*-ITTC with TA treatment, (III) *m*-ITTC with additive treatment, (IV) *m*-ITTC with additive and TA treatment. (d) Corresponding line-cut profiles of the GIWAXS patterns of the neat *m*-ITTC film.

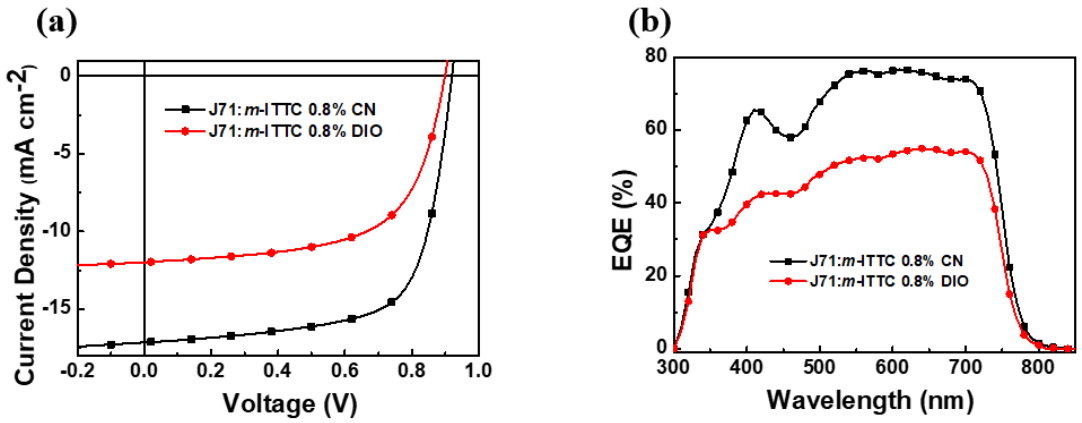

Figure S7. (a) *J-V* characteristics of the OSCs based on J71:*m*-ITTC (1:1.2 w/w, TA 150ºC) with DIO or CN additive treatment under the illumination of AM1.5G, 100 mW cm^{-2}. (b) EQE spectra of the corresponding OSCs.

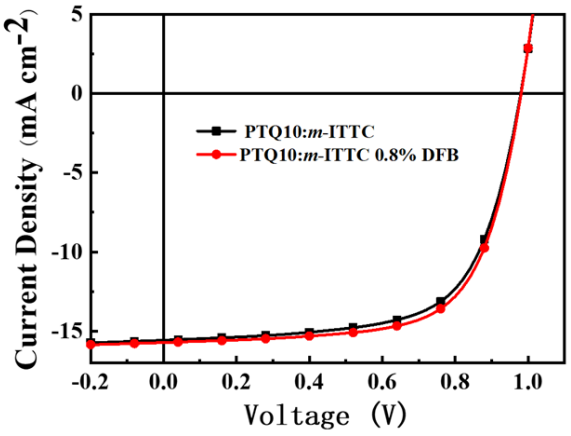

Figure S8. *J-V* characteristics of the OSCs based on PTQ10:*m*-ITTC (1:1.2 w/w, TA 150°C,2min) with DFB additive under the illumination of AM1.5G, 100 mW cm^{-2}.

References

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