

Supplementary Information

TCNQ as Volatilizable Morphology Modulator Enables Enhanced Performance in Non-Fullerene Organic Solar Cells

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Experimental data

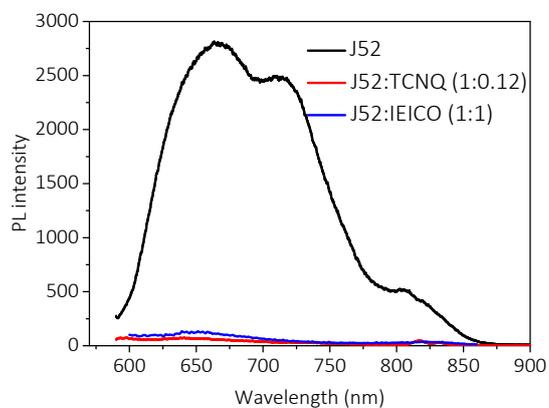


Fig. S1 Photoluminescence spectra excited at 535 nm of the pristine J52, J52 with 12 wt.% TCNQ and J52:IEICO (1:1) films.

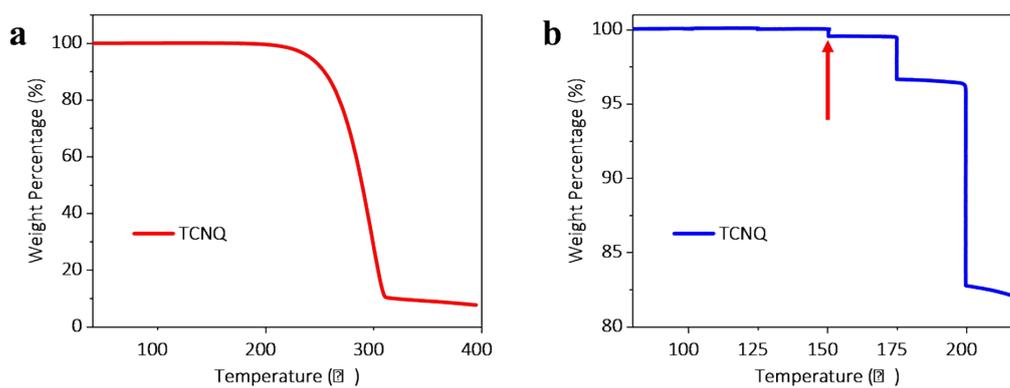


Fig. S2 a) TGA plot of TCNQ at a scan rate of 10 °C/min. b) designed TGA measurements, where the heating temperature is held for 1 h every 25 °C from 100 to 200 °C.



Fig. S3 Picture of TGA crucible after the heating and cooling process of TCNQ.

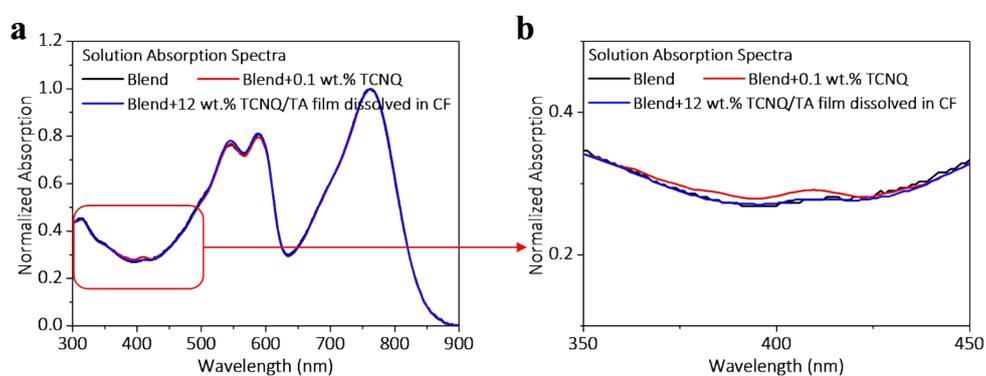


Fig. S4 Normalized absorption spectra of J52:IEICO solution, J52:IEICO+0.1 wt.% TCNQ solution and chloroform (CF) dissolved solution of the annealed J52:IEICO+12 wt.% TCNQ film. These results further prove the complete volatilization of TCNQ after thermal annealing.

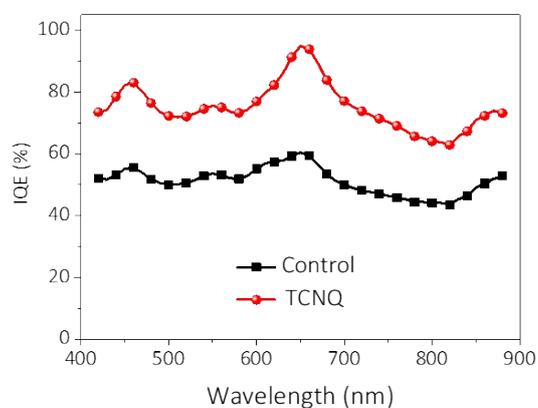


Fig. S5 IQE curves of the control and TCNQ devices.

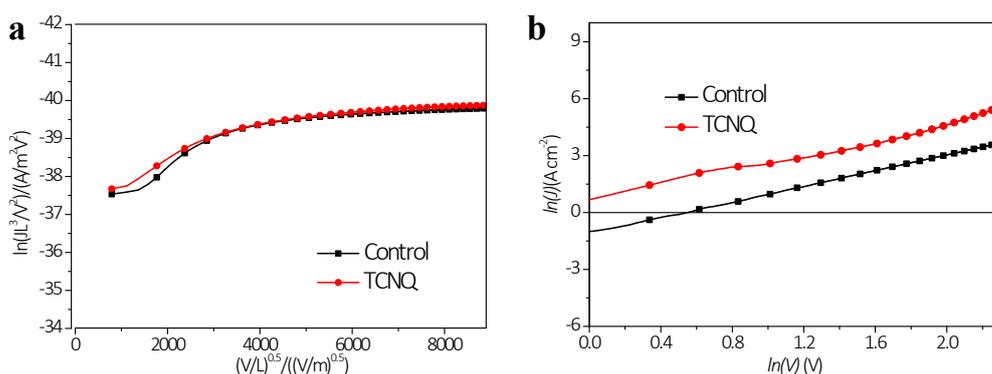


Fig. S6 a) $\ln(JL^3/V^2)$ versus $(V/L)^{0.5}$ and **b)** $\ln(J)$ versus $\ln(V)$ plots of binary and ternary blend films by SCLC method.

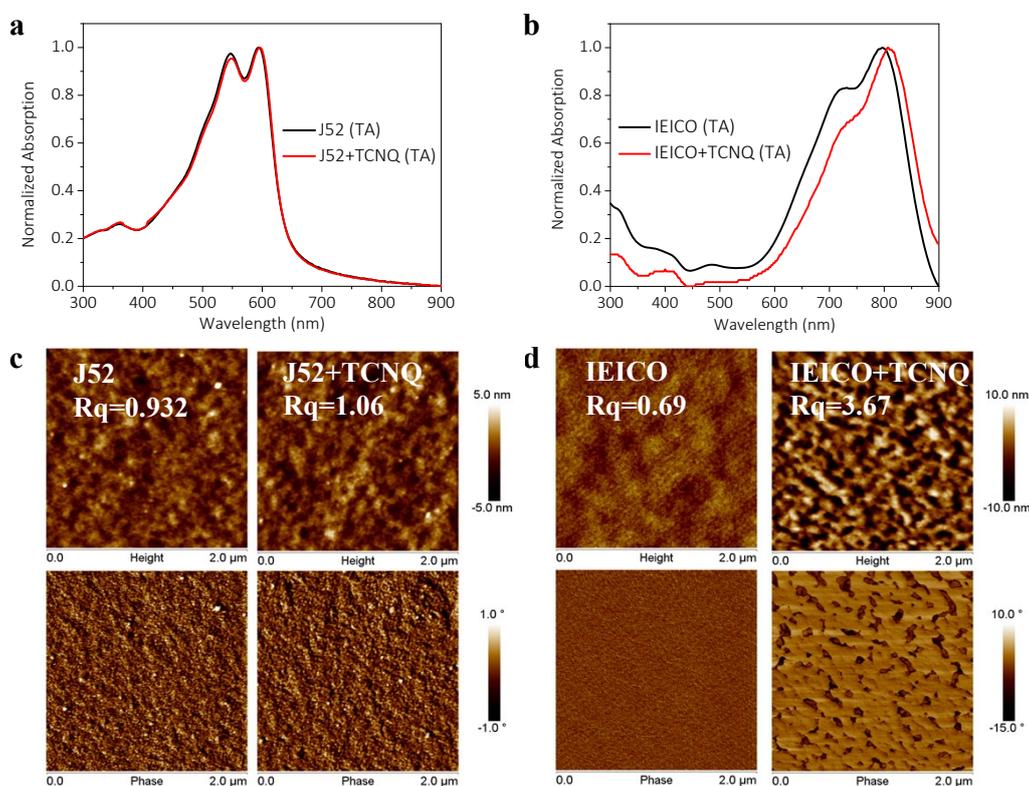


Fig. S7 a) Normalized absorption of J52 and J52+TCNQ films. **b)** Normalized absorption of IEICO and IEICO+TCNQ films. **c)** AFM height and phase images of J52 and J52+TCNQ films. **d)** AFM height and phase images of IEICO and IEICO+TCNQ films. All the films are treated with thermal annealing at 150 °C for 10 min.

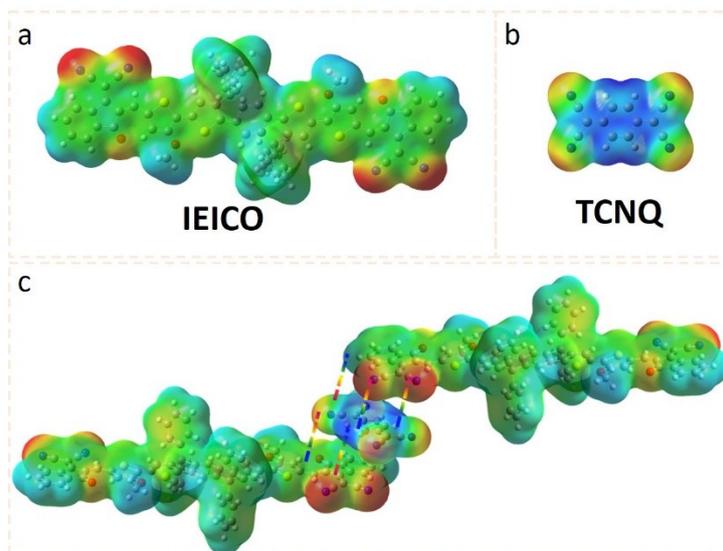


Fig. S8 ESP distribution of **a)** IEICO and **b)** TCNQ. **c)** The proposed assembled geometry structure of IEICO and TCNQ, between which the dot lines represent the intermolecular electrostatic interactions.

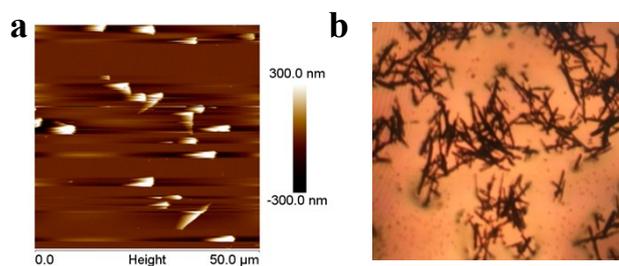


Fig. S9 a) AFM height images and **b)** microphotographs of J52:IEICO+TCNQ blend film without thermal annealing.

Table S1 Photovoltaic parameters of J52:IEICO-based devices processed with different content of solvent additives.

Additives	Voc [V]	Jsc [mA cm ⁻²]	FF	PCE [%]
DIO 0.5% v/v	0.845	12.13	0.609	6.24
DIO 1% v/v	0.841	12.33	0.626	6.49
DIO 3% v/v	0.834	10.33	0.589	5.07

DIO 5% v/v	0.764	9.83	0.534	4.01
CN 0.5% v/v	0.847	14.50	0.599	7.35
CN 1% v/v	0.840	15.69	0.612	8.06
CN 3% v/v	0.835	10.04	0.613	5.13
CN 5% v/v	0.792	5.98	0.535	2.57

^aAll the devices are processed with thermal annealing at 150 °C for 10 min.

Table S2 Photovoltaic parameters of TCNQ-processed (12 wt.%) devices based on J52:IEICO under different thermal annealing conditions.

Temperature [°C]	Time [min]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	PCE [%]
90	10	0.761	4.23	0.252	0.81
100	10	0.801	12.11	0.457	4.43
110	10	0.803	12.40	0.508	5.06
120	10	0.819	15.24	0.523	6.53
130	10	0.823	16.41	0.520	7.02
140	10	0.827	17.98	0.528	7.85
150	0.5	0.690	0.71	0.295	0.14
150	1	0.717	11.21	0.451	3.62
150	3	0.834	15.33	0.521	6.66
150	5	0.829	16.96	0.525	7.38
150	8	0.827	17.61	0.531	7.73

Table S3 Hansen solubility parameters of TCNQ and IEICO.

	δ_d	δ_p	δ_h^a
TCNQ	18.2	18	7.5
IEICO	23.1	4.47	5.07

^a δ_d , δ_p , and δ_h represent the dispersive, polar and hydrogen bonding forces, respectively.

Table S4 Photovoltaic parameters of TCNQ-processed devices based on different active layers.

Active layer (D/A ratio)	Condition ^a	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	PCE [%]
J52:IEICS ^b (1:1.2)	Control	0.879	15.25	0.509	6.82
	TCNQ	0.836	17.98	0.588	8.76

PBDB-TF:Y6	Control	0.820	24.21	0.731	14.49
(1:1.2)	TCNQ	0.801	25.13	0.717	14.43
PBDB-TF:IT-4F	Control	0.878	18.93	0.712	11.83
(1:1)	TCNQ	0.835	19.34	0.704	11.37
J52:ITM	Control	0.851	18.89	0.652	10.48
(1:1)	TCNQ	0.818	19.22	0.624	9.81
PBDB-T:PC ₇₁ BM	Control	0.845	10.60	0.452	4.05
(1:1.5)	TCNQ	0.816	9.83	0.434	3.48

^a 12 wt.% of TCNQ was added in each blend solution and all the active layers were treated with thermal annealing at 150 °C for ten minutes. As-cast devices without using any additives are used as control devices. IEICS is one of the analogs of IEICO, which has not been reported yet, and its chemical structure is shown in Fig. S9.

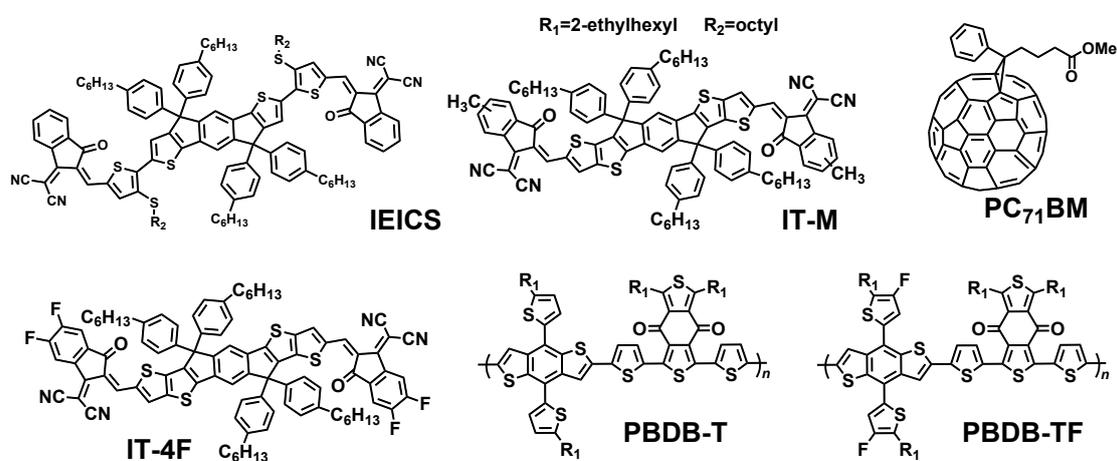


Fig. S9 Chemical structures of other active layer materials applied in this work.

Materials

IEICO was synthesized in our laboratory according to the previous work.^[1] J52 was purchased from Solarmer Material Inc. TCNQ and the other materials were common commercial level and used as received.

Device fabrication

All the OSC devices were fabricated and characterized by using a conventional device structure of ITO/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS)/active layer/poly[(9,9-bis(3'-((N,N-dimethyl)-N-ethyl-ammonium)-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)]dibromide (PFN-Br)/Al, in which PEDOT:PSS and PFN-Br served as the hole-transport layer and electron-transport layer, respectively. The washed ITO glasses were first treated by UV-ozone for 15 minutes. PEDOT:PSS solution was spin-coated onto the ITO substrate at a speed of 3,000 r.p.m. for 30 seconds and then the ITO substrates were placed on a hot plate for 15 min at 150 °C. The weight ratio of donor:acceptor for J52:IEICO was kept at 1:1.2 and the J52:IEICO blend was dissolved in chlorobenzene solvent at a polymer weight concentration of 12 mg/mL. The blend solution was stirred on a hot plate at 60 °C for 5 h. TCNQ of 10 mg/mL was dissolved in THF. After adding different weight ratios of TCNQ, the blend solution was stirred for more than 30 min. The blend solution was spin-coated at 1200 r.p.m for 60 s to obtain a film thickness of about 100 nm and then thermal annealing for 10 min at 140 °C was utilized to optimize the morphology of the active layer. Then PFN-Br was coated on the top of the active

layer at 3000 rpm for 30 s. Finally, about 90 nm of Al with an area of 3.7 mm² were deposited onto the active layer under high vacuum. Except for the spin-coating of PEDOT:PSS, the other the processes were all carried out in N₂-filled glovebox.

Instruments and Measurement

AM 1.5 G spectrum at 100 mW cm⁻² along with a National Institute of Metrology, China calibrated reference cell was used to measure the *J-V* plots of OSCs. The EQE spectrum was recorded by an integrated quantum efficiency measurement system (QE-R3011, Enli Technology Co. Ltd., Taiwan), which was calibrated with a crystal silicon photovoltaic cell ahead of the measurement.

Absorption spectra of diluted solutions (dissolved in chloroform) and films (spin-coated on quartz substrates) were measured on a Hitachi UH4150 UV-Vis spectrophotometer. The thickness of blend layers was measured via the surface profilometer Bruker Dektak XT. Thermogravimetric analysis (TGA) was measured on a Pyris 1 TGA under a nitrogen flow. X-ray diffraction (XRD) patterns were collected using a Rigaku D/max 2500 X-ray diffractometer and the samples were prepared on Si substrates by drop-casting. AFM images were obtained by a Nanoscope V AFM in tapping mode. TEM images were performed on a JEOL 2200FS instrument at 160 KV accelerating voltage in bright field mode.

Reference

1. H. Yao, Y. Chen, Y. Qin, R. Yu, Y. Cui, B. Yang, S. Li, K. Zhang, J. Hou, *Adv. Mater.*, **2016**, *28*, 8283.