Efficient Inverted Quasi-Bilayer Organic Solar Cells Fabricated by Using Non-Halogenated Solvent Processes

Jung-Hao Chang,[a] Hsiao-Fang Wang,[b] Wei-Chieh Lin,[a] Kai-Ming Chiang,[a] Kuan-Chen Chen,[a] Wei-Ching Huang,[a] Zheng-Yu Huang,[a] Hsin-Fei Meng,[c] Rong-Ming Ho[b] and Hao-Wu Lin[a]*

[a]Department of Materials Science and Engineering, National Tsing Hua University, No. 101, Section 2, Kuang-Fu Road, Hsinchu, Taiwan 30013.

[b]Department of Chemical Engineering, National Tsing Hua University, No. 101, Section 2, Kuang-Fu Road, Hsinchu, Taiwan 30013.

[c]Institute of Physics, National Chiao Tung University, Hsinchu, Taiwan 30013.

Supporting Information

Contents

PBDTTT-C-T thin film drying time

Table S1. Drying times of PBDTTT-C-T thin films.

Toluene:*o*-xylene (wt%)	Time (s)
100:0	0.2
95:5	0.4
90:10	0.6
80:20	0.9

Donor layer thickness corresponding to blade-coating speed

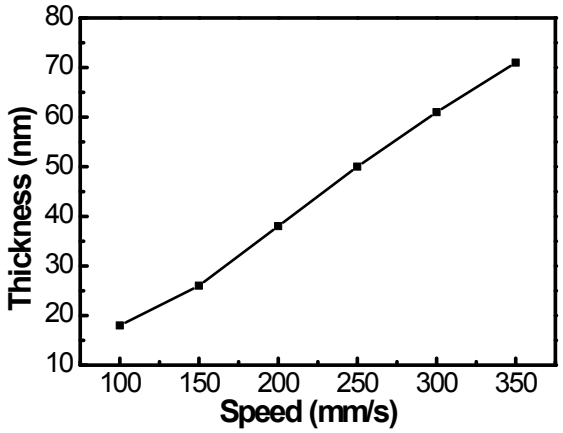

Figure S1. PBDTTT-C-T layer thickness versus blade-coating speed.

Optical constants of thin-films

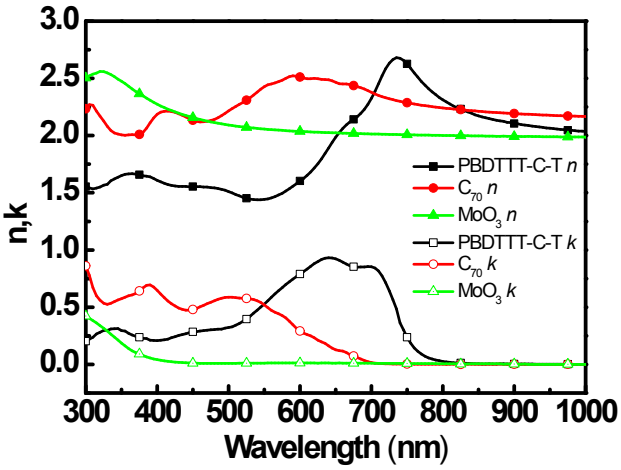

Figure.S2. Optical constants of **PBDTTT-C-T** (squares), **C_{70}** (circles) and **MoO_3** (triangle) thin-film spectra.

Performance of devices with varying PBDTTT-C-T layer thickness

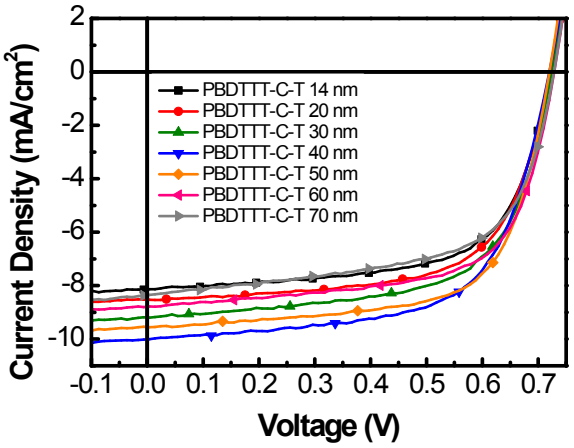

Figure S3. *J*-V characteristics of devices with various PBDTTT-C-T thicknesses under simulated 1 sun AM1.5G illumination.

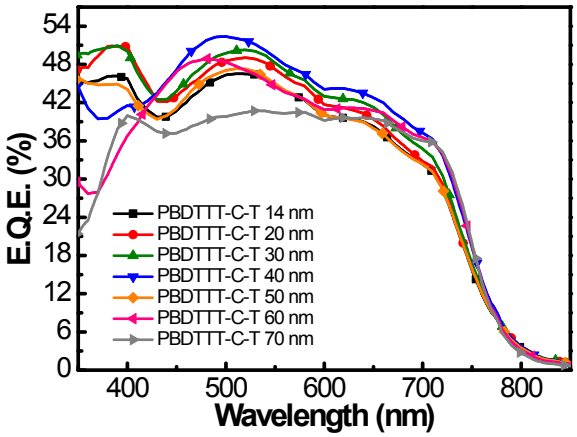

Figure S4. External quantum efficiency spectra of devices with various PBDTTT-C-T thicknesses.

Table S2. Summary of device performances of cells with various PBDTTT-C-T thicknesses

Thickness of PBDTTT-C-T	V_{OC}(V)	J_{SC}(mA/cm^2)	FF	PCE(%)
14 nm	0.72	9.21	0.64	4.28
20 nm	0.72	9.72	0.65	4.56
30 nm	0.72	10.03	0.64	4.74
40 nm	0.72	11.02	0.64	5.08
50 nm	0.72	10.46	0.67	4.98
60 nm	0.73	9.81	0.65	4.91
70 nm	0.73	9.50	0.61	4.23

AFM results of the C_{70} neat film and C_{70}/PBDTTT-C-T films

Table S3. Surface roughness characteristics of the C_{70} neat film and C_{70}/PBDTTT-C-T films (toluene:*o*-xylene = 100:0, wt%), (toluene:*o*-xylene = 95:5, wt%), and (toluene:*o*-xylene = 80:20, wt%).

	R_{rms} (nm)	R_{max} (nm)
C_{70} neat film	0.9	11.7
PBDTTT-C-T neat film	0.8	10.8
C_{70}/PBDTTT-C-T (toluene:*o*-xylene = 100:0, wt%)	4.5	32.9
C_{70}/PBDTTT-C-T (toluene:*o*-xylene = 95:5, wt%)	9.2	61.2
C_{70}/PBDTTT-C-T (toluene:*o*-xylene = 80:20, wt%)	20.1	156.7

TEM images of the C_{70} neat film and C_{70}/PBDTTT-C-T films

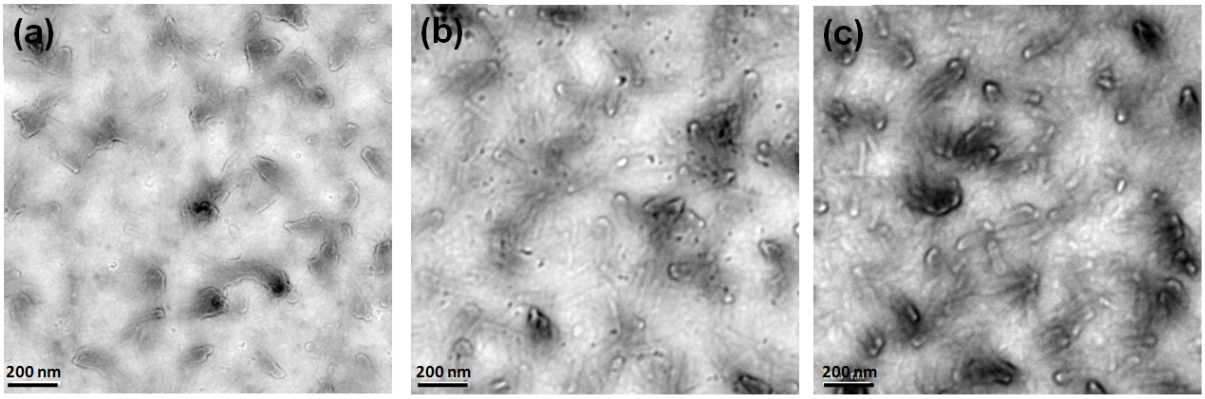

Figure S5. Defocused TEM micrographs of C_{70}/PBDTTT-C-T with (a) (toluene:*o*-xylene = 100:0, wt%), (b) (toluene:*o*-xylene = 95:5, wt%) and (c) (toluene:*o*-xylene = 80:20, wt%) thin films.

Top view SEM and AFM images of donor PBDTTT-C-T neat film

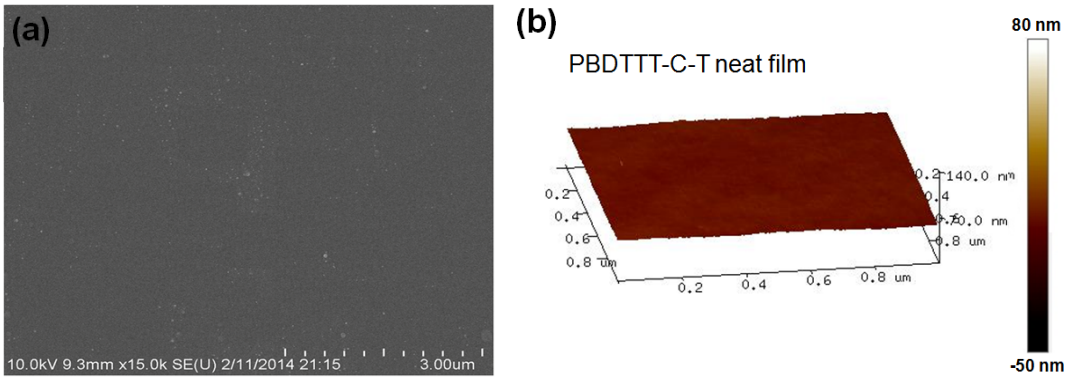

Figure S6. Top view SEM image of ITO/PEDOT:PSS (40 nm)/PBDTTT-C-T (toluene:*o*-xylene = 95:5, wt%) and AFM image of ITO/PBDTTT-C-T (toluene:*o*-xylene = 95:5, wt%).

Cross-section TEM images of the (toluene:o-xylene = 95:5, wt%) film

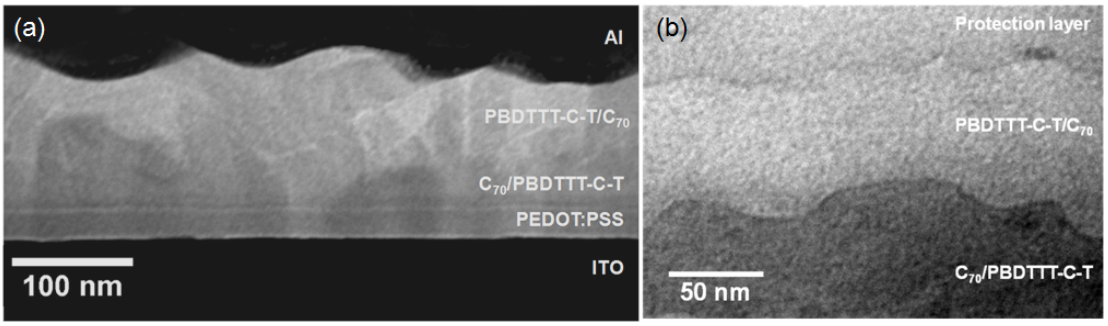

Figure S7. (a) Method 1: Cross-sectional TEM image (15000x) of ITO/PEDOT:PSS (40 nm)/C_{70} (60 nm)/PBDTTT-C-T (toluene:*o*-xylene = 95:5, wt%)/Al. (b) Method 2: Cross-sectional TEM image of C_{70} (60 nm)/PBDTTT-C-T (toluene:*o*-xylene = 95:5, wt%).

Method 1: Prior to TEM imaging, the cross-section of the (toluene:*o*-xylene = 95:5, wt%) device was sliced by a focused ion beam (FIB). In this study, the FIB sample preparation condition was as following: before FIB cutting, a protection layer (~200 nm) was deposited and low accelerating voltage (5 KeV) was used to reduce milling damage. With appropriate sectioning conditions, the problems of the deformation and damage to soft material can be significantly alleviated.[1] A cross-section (8 μm wide by 5 μm tall by ~60 nm thick) sample was cut, attached to an Omniprobe copper lift-out grid for TEM imaging.The FIB sample preparation procedure was modified for use the FEI Helios Nanolab 400 Dual Beam FIB with Gallium ion source and integrated OmniprobeAutoprobe 200 nanomanipulater.

Method 2: To examine the cross-sectional morphology, the thin films were prepared by immersing the glass/PEDOT:PSS/C_{70}/PBDTTT-C-T samples into deionized water. After dissolution of PEDOT:PSS, the C_{70}/PBDTTT-C-T films floated onto the water surface. They were then picked up with a piece of polyimide thin plate and transferred into an oven for 6 hours at 80 degree to evaporate the residual water. Before embedding with epoxy resin, samples were sputter-deposited with 5 nm carbon as stabilizer. The epoxy-embedded thin-film samples were microtomed normal to the film plane with a thickness of 50 nm and transferred onto a Cu grid. A JEOLJEM-2100 transmission electron microscope was used at an accelerating voltage of 200 kV.[2]

1. J. S. Moon, C. J. Takacs, Y. Sun and A. J. Heeger, *Nano Lett.*, 2011, **11**, 1036.
2. M. S. She, T. Y. Lo and R. M. Ho, *ACS Nano*, 2013, **7**, 2000.

Performance of devices with a CsF cathode

Devices were fabricated with the following structure: ITO/CsF (1 nm)/C_{70} (60 nm)/PBDTTT-C-T (toluene:*o*-xylene = 95:5, wt%)/MoO_3 (10 nm)/Ag (110 nm). CsF was deposited in a high vacuum chamber with a base pressure ~1×10^{-6} Torr.

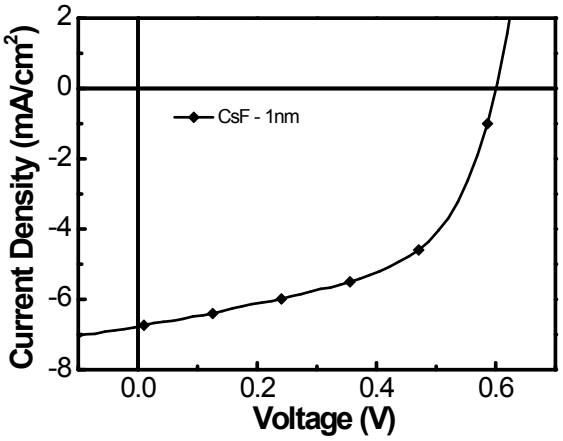

Figure S8. *J-V* characteristics of the device with a CsF cathode under 1 sun simulated AM 1.5G solar illumination.

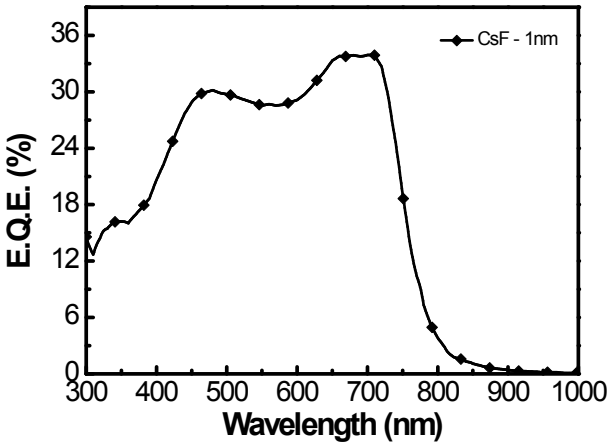

Figure S9. External quantum efficiency spectrum of the device with a CsF cathode.

Table S4. Device performance of cells with a CsF cathode.

CsF	V_{OC}(V)	J_{SC}(mA/cm^2)	FF	PCE(%)
1 nm	0.60	6.70	0.53	2.17

Performance of devices with various ZnO layer thicknesses

Devices were fabricated with the following structure ITO/ZnO/C_{70} (60 nm)/PBDTTT-C-T (toluene:*o*-xylene = 95:5, wt%)/MoO_3 (10 nm)/Ag (110 nm). A zinc acetate [Zn(ac)] solution (7.3 g/L) in 96% 2-methoxy ethanol and 4% ethanolamine was spin coated at different rpms (1000 – 8000) onto pre-cleaned ITO-coated glass substrates to form ZnO sol-gel films. The ZnO sol-gel films were then annealed in air at 150° C for 5 min.

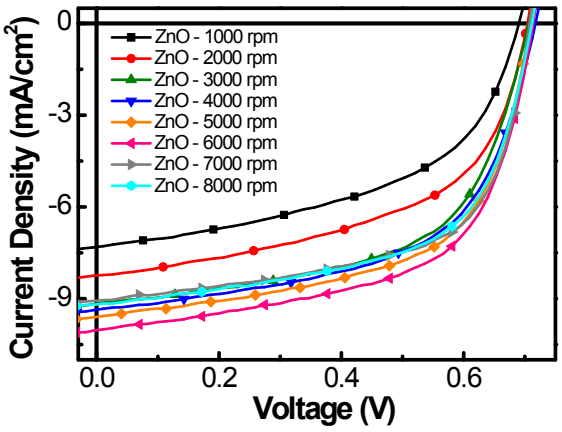

Figure S10. *J*-V characteristics of devices with various ZnO thicknesses.

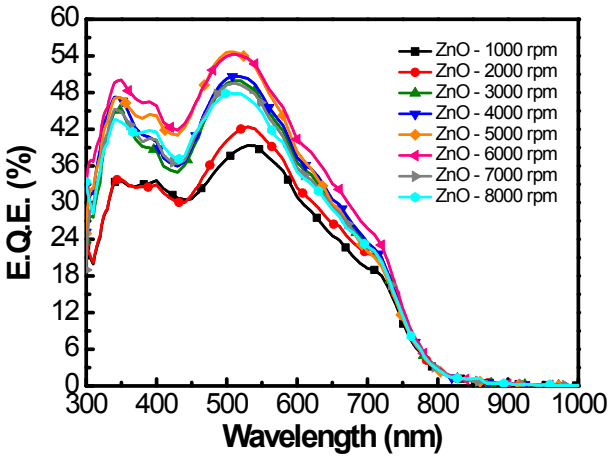

Figure S11. External quantum efficiency spectra of devices with various ZnO thickness.

Table S5. Summary of device performances of cells with varying ZnO thickness.

ZnO (r.p.m.)	V_{OC}(V)	J_{SC}(mA/cm^2)	FF	PCE(%)
1000 rpm	0.69	7.32	0.51	2.55
2000 rpm	0.70	8.23	0.54	3.11
3000 rpm	0.71	9.14	0.58	3.76
4000 rpm	0.72	9.41	0.57	3.83
5000 rpm	0.71	9.61	0.59	4.03
6000 rpm	0.71	10.34	0.60	4.27
7000 rpm	0.71	9.16	0.62	3.96
8000 rpm	0.71	9.29	0.59	3.89

Device performance of PTB7 cells

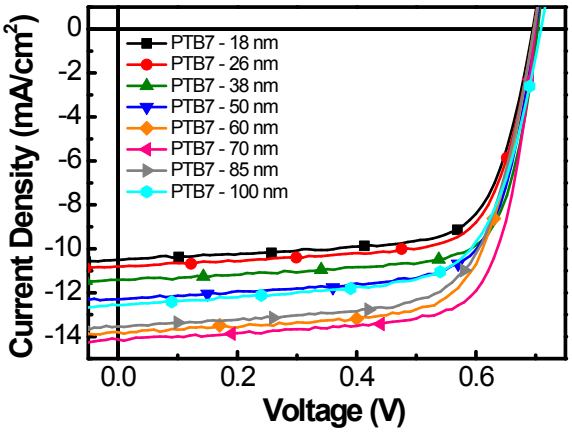

Figure S12. *J-V* characteristics of devices with various PTB7 thicknesses.

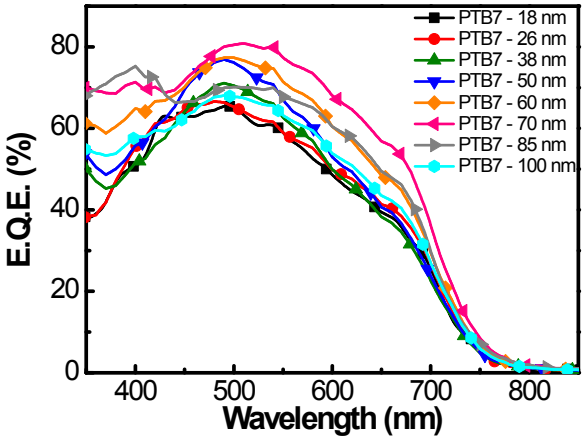

Figure S13. External quantum efficiency spectra of devices with various PTB7 thicknesses.

Table S6. Summary of performance parameters for devices with various PTB7 thicknesses.

Thickness of PTB7	V_{OC}(V)	J_{SC}(mA/cm^2)	FF	PCE(%)
18 nm	0.69	11.10	0.71	5.52
26 nm	0.70	11.44	0.72	5.68
38 nm	0.70	12.32	0.74	6.42
50 nm	0.70	13.37	0.71	6.58
60 nm	0.70	13.86	0.70	6.72
70 nm	0.70	14.14	0.73	7.15
85 nm	0.70	13.52	0.68	6.46
100 nm	0.71	12.51	0.68	6.03

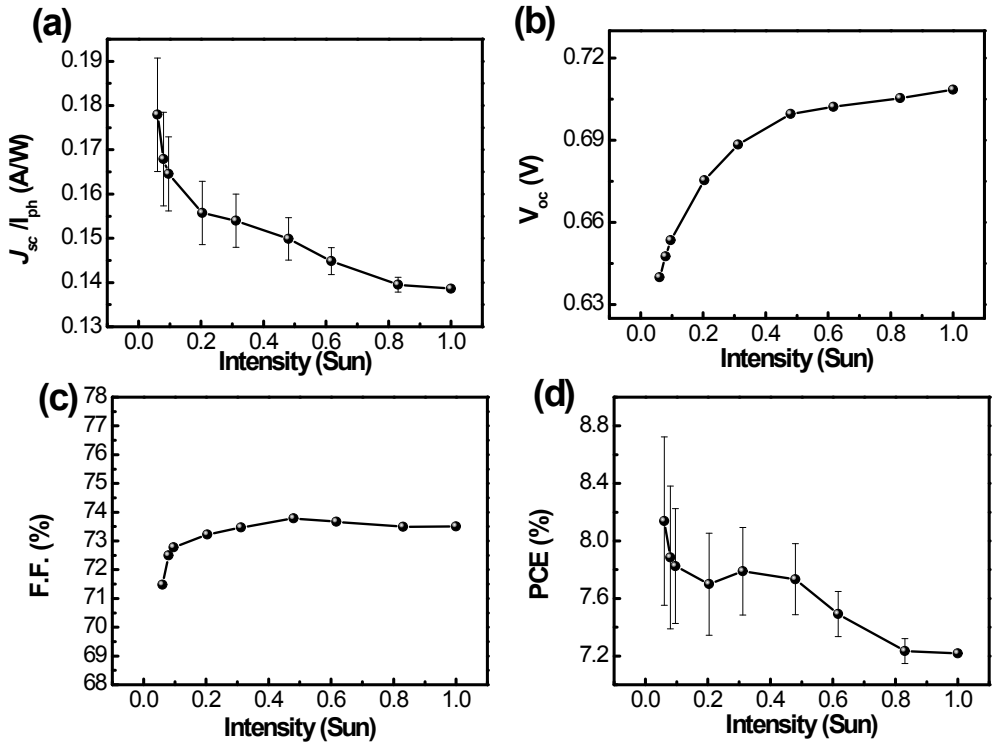

Figure S14. PTB7 device (PTB7 thickness = 70 nm) performance parameters under various light intensities. I_{ph}: incident light intensity, unit: W/cm^2.

Table S7. Summary of cell performance parameters under various light intensities.

Light intensity (Sun)	V_{OC} (V)	J_{SC}/I_{ph} (A/W)	FF (%)	PCE (%)
0.06	0.639	0.178	71.4	8.13
0.08	0.647	0.168	72.5	7.88
0.1	0.653	0.165	72.7	7.82
0.2	0.675	0.156	73.2	7.70
0.3	0.688	0.154	73.4	7.79
0.5	0.699	0.150	73.7	7.73
0.62	0.702	0.145	73.6	7.49
0.83	0.705	0.140	73.5	7.23
1	0.708	0.139	73.5	7.22