Supporting Information for

Efficient as-cast bulk-heterojunction solar cells based on a *tert*-butyl substituted methanofullerene acceptor

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General Remarks. A CHI 660c electrochemical workstation was used to carry out the cyclic voltammetry (CV) experiments. The measurements were conducted in all glass cells thermostated at 25 °C and under an Ar atmosphere. A mixture 4:1 of acetonitrile (ACN) and o-dichlorobenzene (ODCB) was used as solvent. ACN was freshly distilled over CaH_2 while ODCB was used as received. Tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6, Fluka, 99%) was employed as the supporting electrolyte after being recrystallized from ethanol. The working electrode was an homemade glassy-carbon (Tokai GC-20) disc (1.1 mm diameter) while a platinum plate was used as the counter electrode and an Ag/AgCl electrode as reference. At the end of the experiment some ferrocene (Fc, Carlo Erba) was added to the solution in order to have an internal standard and calibrate the measured potential against the ferricenium/ferrocene (Fc^+/Fc) couple. In order to minimize the ohmic drop between the working and the reference electrodes the CVs were recorded using a feedback correction.

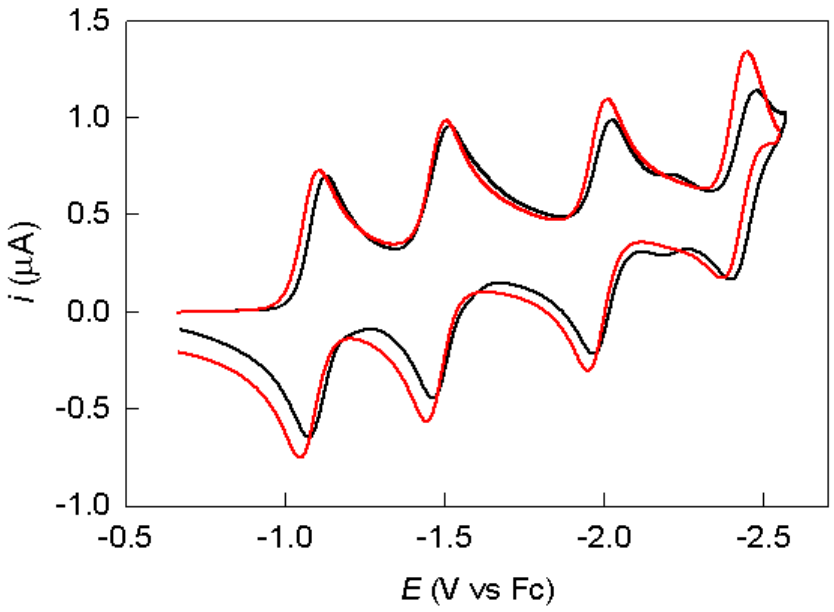

Figure S1. Background subtracted cyclic voltammetries of **PCBtB** (black line) and **PCBM** (red line) in o-dichlorobenzene/acetonitrile (4:1), Bu_4NPF_6 0.1 M on a glassy carbon electrode. C = 0.40 mM, scan rate = 0.1 V s^{-1}.

Table S1. Bulk-heterojunction photovoltaic parameters of P3HT:PCBtB (or PCBM) based solar cells.

Active Layer[a] D:A ratio [wt/wt]	**Total Conc.** [mg/mL]	$T_{ann.}$ [°C][b]	V_{OC} [mV]	J_{SC} [mA/cm^2]	**FF** [%]	**PCE** [%]
P3HT**:PCBtB** (1.2:1)	37	150	430	2.57	42	0.47
P3HT**:PCBtB** (1:1)	28	--	542	5.88	51	1.63
P3HT**:PCBtB** (1:1)	34	80	517	5.03	50	1.30
P3HT**:PCBtB** (1:1)	40	--	532	4.07	51	1.11
P3HT**:PCBtB** (1:1)	40	110	466	4.19	50	0.98
P3HT**:PCBtB** (0.88:1)	32	80	484	6.56	52	1.65
P3HT**:PCBtB** (0.88:1)	32	130	462	6.28	50	1.45
P3HT**:PCBtB** (0.88:1)	32	110 (post ann.)	361	5.60	48	0.98
P3HT**:PCBtB** (0.88:1)	32	110 / 20 min	450	5.49	49	1.21
P3HT**:PCBtB** (1:0.6)[c]	24[c]	--	447	3.01	34	0.46
P3HT**:PCBM** (1.2:1)[d]	37	--	576	7.62	64	2.83
P3HT**:PCBM** (1.2:1)[d]	37	110	582	8.27	67	3.22
P3HT**:PCBM** (1:1)[d]	34	--	564	7.32	65	2.70
P3HT**:PCBM** (1:1)[d]	34	110	583	8.18	67	3.21
P3HT**:PCBM** (0.88:1)[d]	32	--	563	6.34	66	2.36
P3HT**:PCBM** (0.88:1)[d]	32	110	563	6.86	67	2.60
P3HT**:PCBM** (0.75:1)[d]	29.8	--	581	4.23	63	1.55
P3HT**:PCBM** (0.75:1)[d]	29.8	110	581	4.82	64	1.80

a) ODCB solutions ; *b)* Annealing time: 10 min; *c)* Chlorobenzene (CB) solution; *d)* Constant concentration of PCBM : 17 mg/mL.

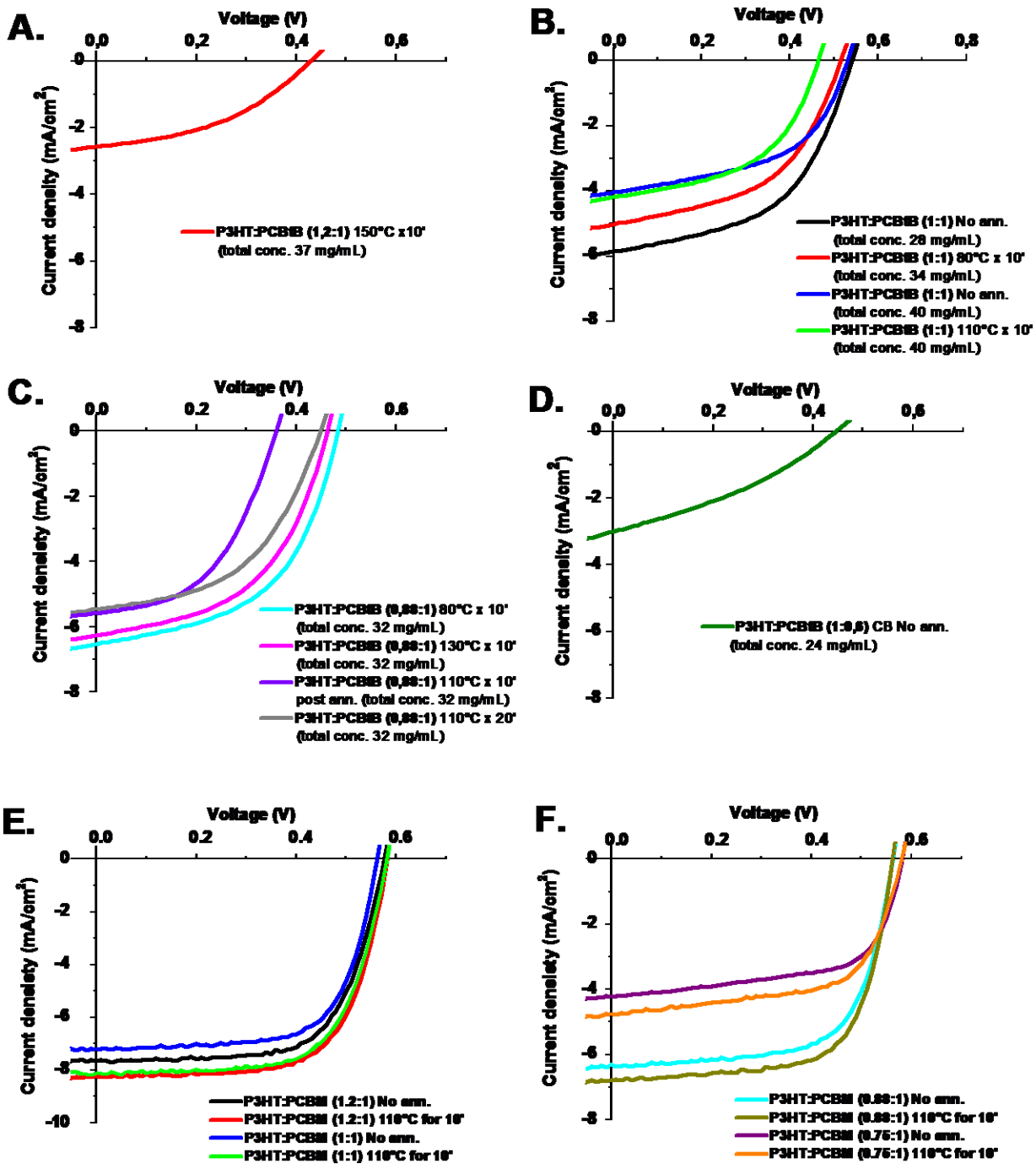

Figure S2. *J-V* plots, under illumination, of the BHJ solar cells reported in Table S1.

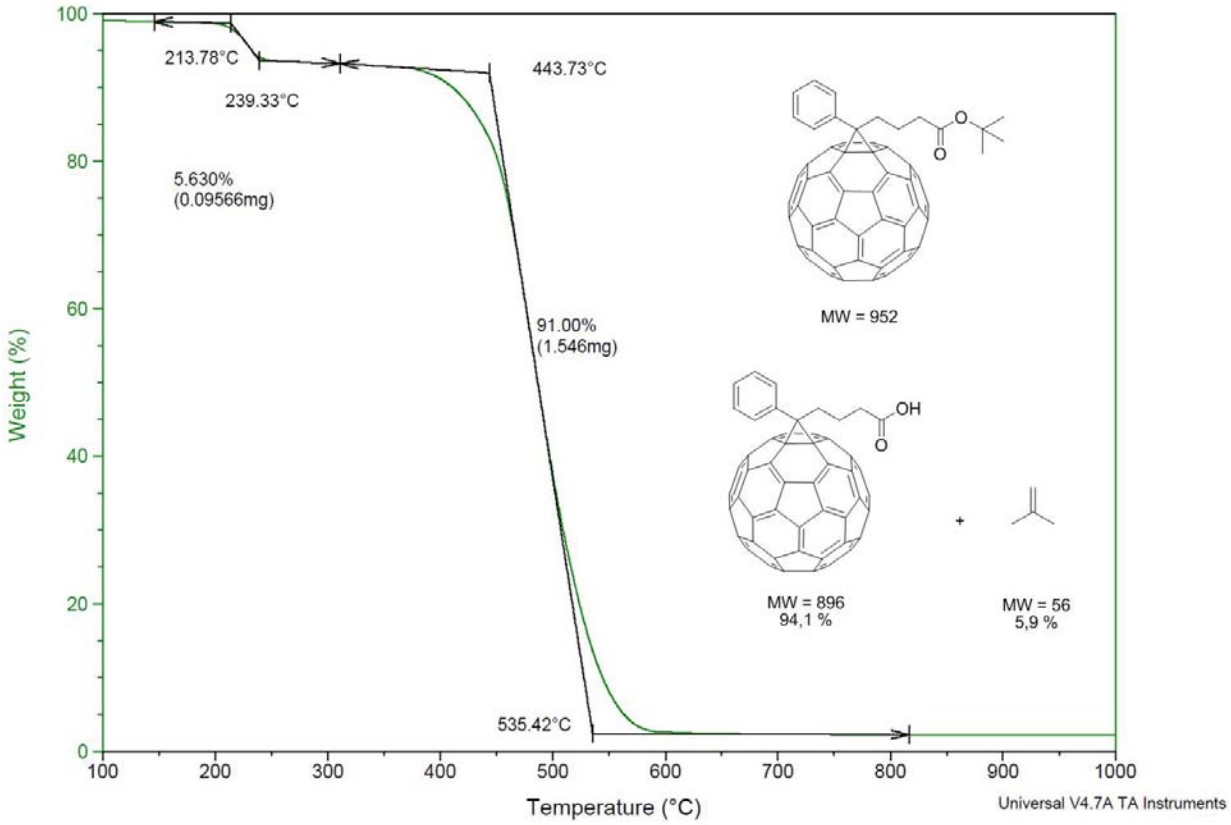

Figure S3. TGA analysis of PCBtB. From the TGA data it is proposed that the first transition that starts at ca 214 C is due to the loss of isobutylene.

Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q5000IR under nitrogen atmosphere from 100 °C to 1000 °C with a heating rate of 10 °C/min.

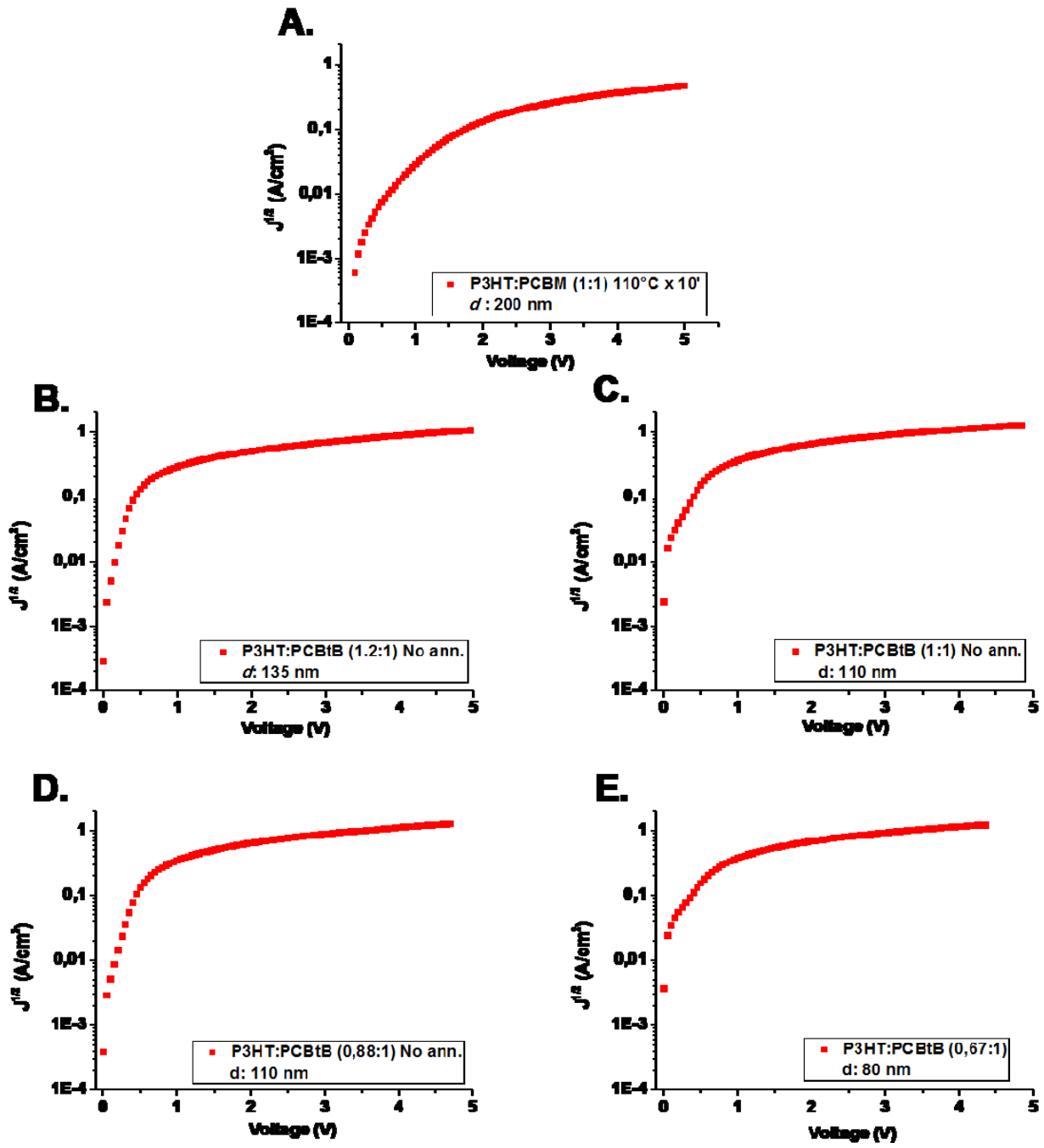

Figure S4 : Dark $J^{1/2}$-V curves of *hole-only devices* based on: (**A**) (1:1) P3HT:PCBM annealed at 110°C x 10' and (**B-E**) P3HT:PCBtB , with different D:A (wt/wt) composition, films. "*d*" is the thickness of the active layer.

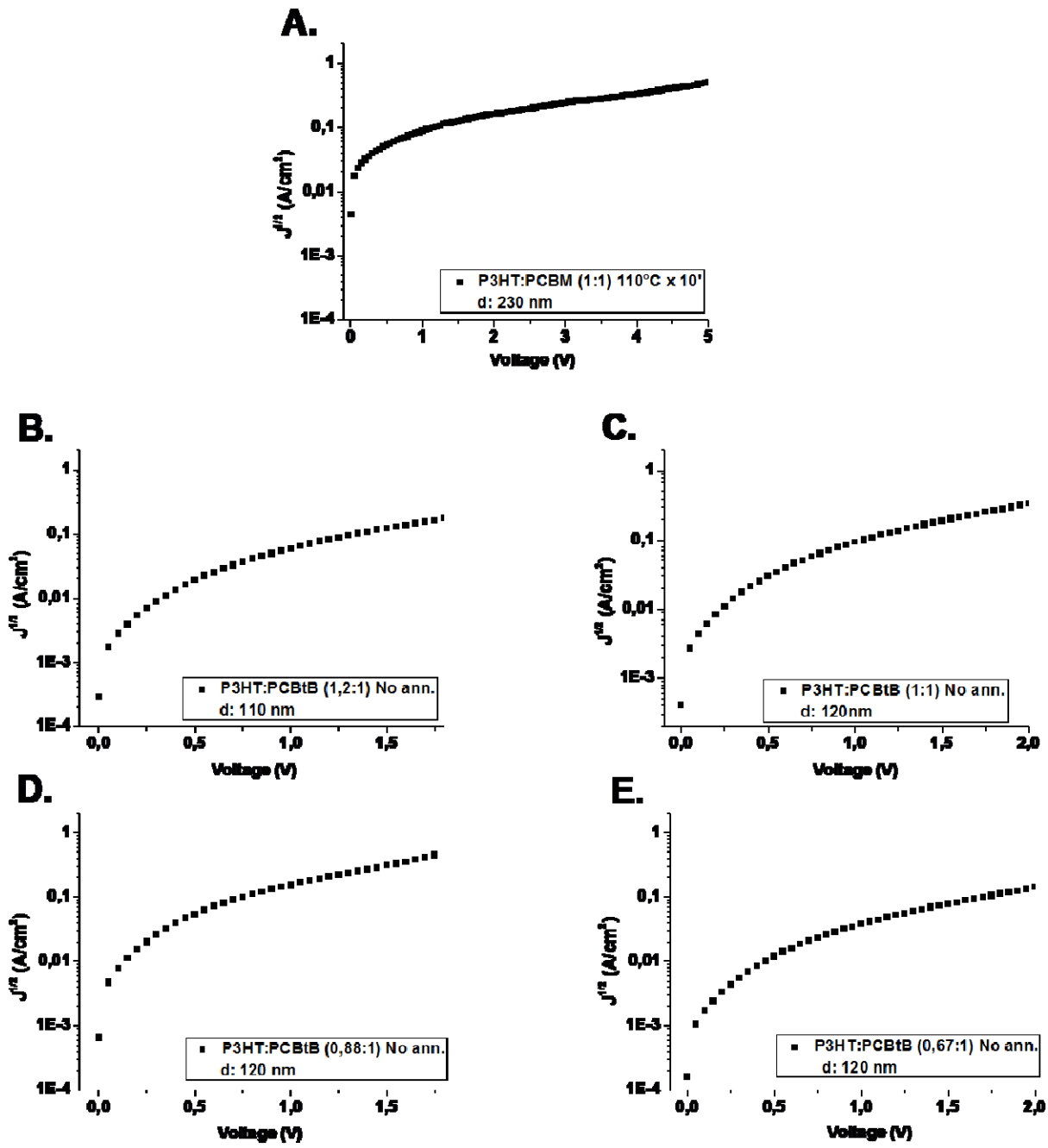

Figure S5 : Dark $J^{1/2}$-V curves of *electron-only devices* based on: (**A**) P3HT:PCBM (1:1) annealed at 110°C x 10' and (**B**-**E**) P3HT:PCBtB , with different D:A (wt/wt) composition, films. "*d*" is the thickness of the active layer.

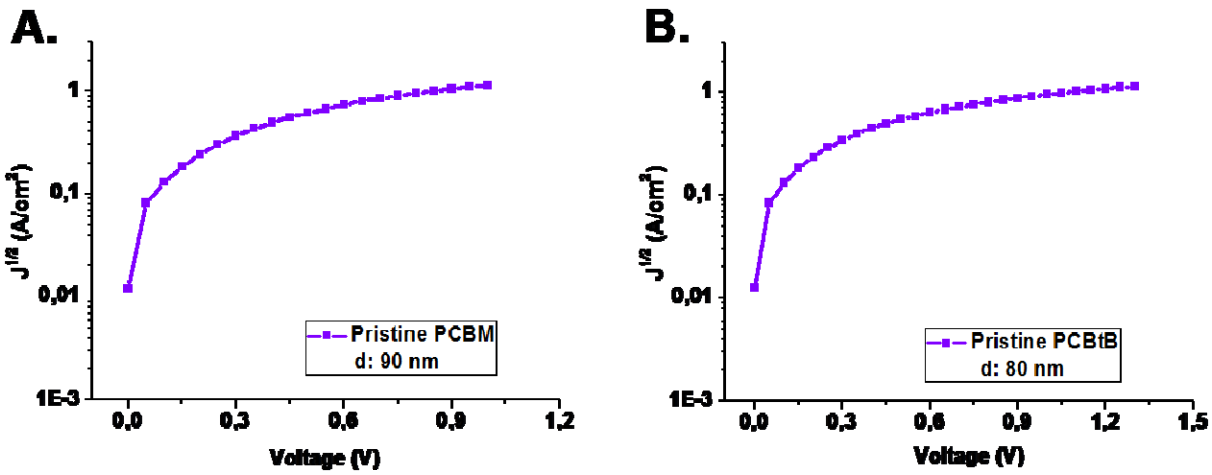

Figure S6 : Dark $J^{1/2}$-V curves of *electron-only devices* based on pristine : (**A**) PCBM and (**B**) PCBtB films spin-coated from ODCB solutions. "*d*" is the thickness of the active layer.