Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information of

The Role of Fullerenes in Environmental Stability of Polymer:Fullerene Solar Cells

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Supplementary Table 1 Summary of device parameters of ITO/PEDOT:PSS/PCDTBT:PCBM(1:2)/Ca/Al devices with different degradation times under simulated AM1.5G illumination in air, before top electrode deposition.

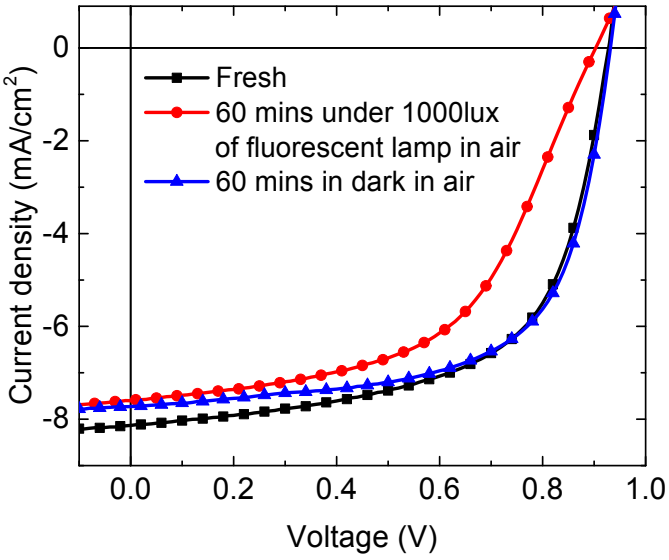
Film degradation time (mins)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0	8.13	0.928	61.5	5.01
10	7.09	0.868	46.5	3.19
30	4.96	0.823	42.4	1.93
60	3.83	0.782	40.5	1.35
600	0.95	0.488	39.5	0.20

Supplementary Table 2 Summary of device parameters of PCDTBT:PCBM devices exposed to air for 60 minutes in the dark and under 1000 lux of compact fluorescent lamp.

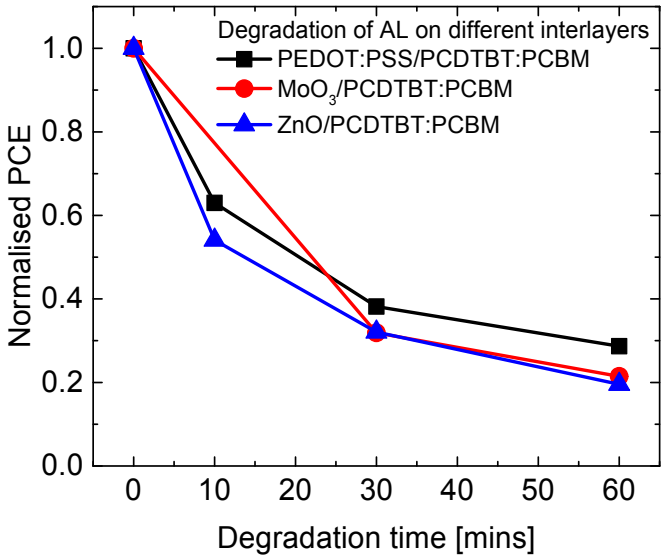
Film degradation condition	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
Fresh	8.13	0.928	61.5	5.01
60 mins under 1000 lux fluorescent lamp in air	7.60	0.903	54.1	4.10
60 mins in dark in air	7.73	0.932	64.5	5.18

Supplementary Table 3 Summary of device parameters of PCDTBT:PCBM blend devices PCDTBT:PCBM blend devices made with different fractions of degraded PCBM, the percentages indicating the relative fraction of O-PCBM in the acceptor phase.

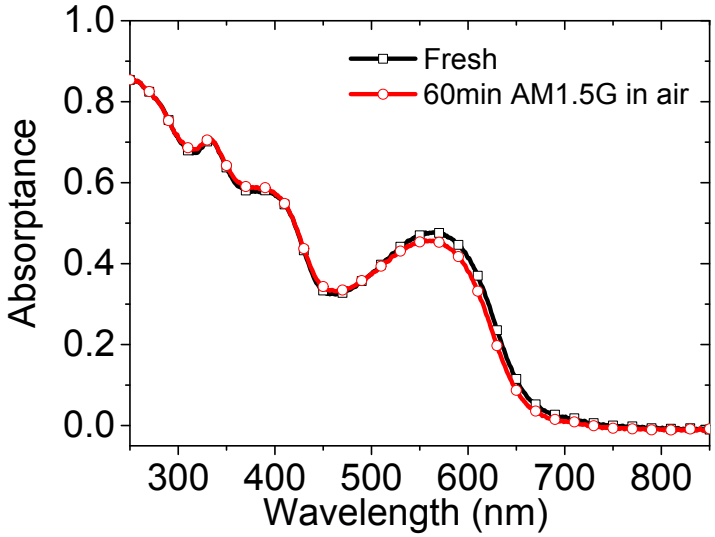
O-PCBM (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0	8.13	0.928	61.5	5.01
0.2	6.76	0.885	51.4	3.69
0.4	6.08	0.852	45.7	2.85
0.9	4.42	0.795	42.2	1.78
1.8	3.17	0.740	42.0	1.18
3.6	2.14	0.617	39.8	0.63



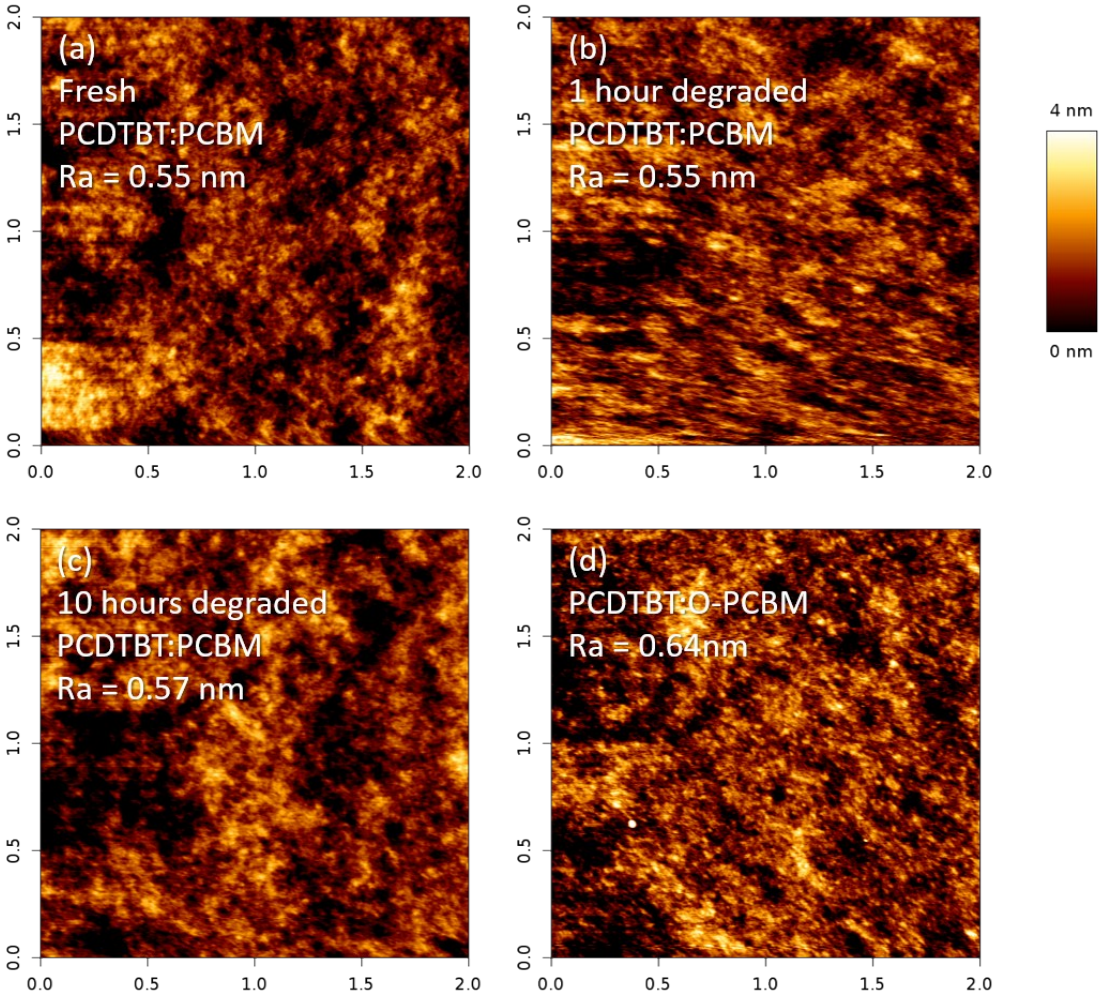
Supplementary Figure 1 *J–V* characteristic of PCDTBT:PCBM devices exposed to air for 60 minutes in the dark and under 1000 lux of compact fluorescent lamp.



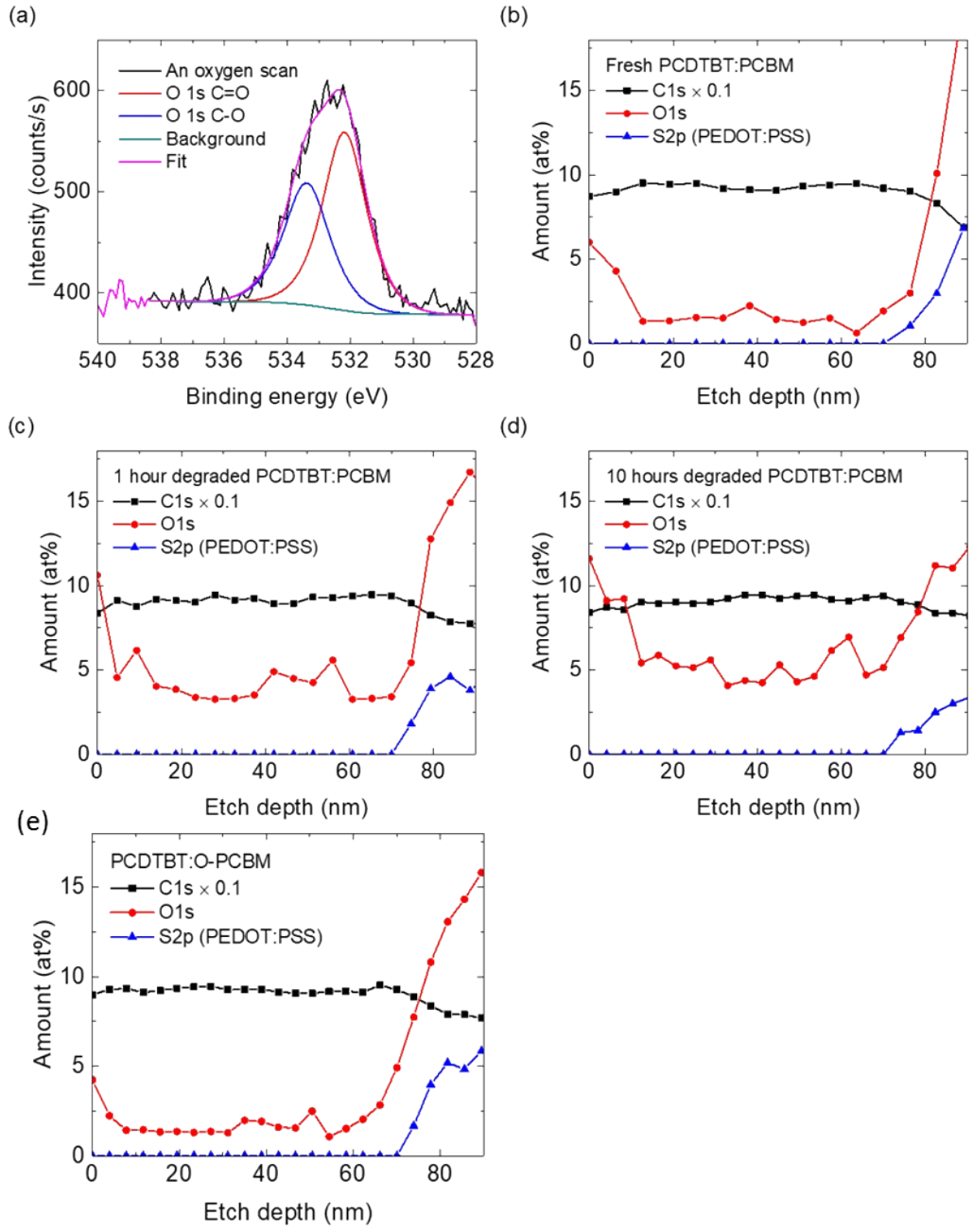
Supplementary Figure 2 Normalised PCE of PCDTBT:PCBM devices with active layers degraded on different interlayers, PEDOT:PSS, MoO_3, and ZnO. The devices using PEDOT:PSS and MoO_3 are finished by Ca/Al as top electrode; the devices using ZnO are finished by MoO_3/Ag as top electrode. The PCEs of the fresh devices using PEDOT:PSS, MoO_3, and ZnO are 5.01%, 4.73%, and 4.43%, respectively.



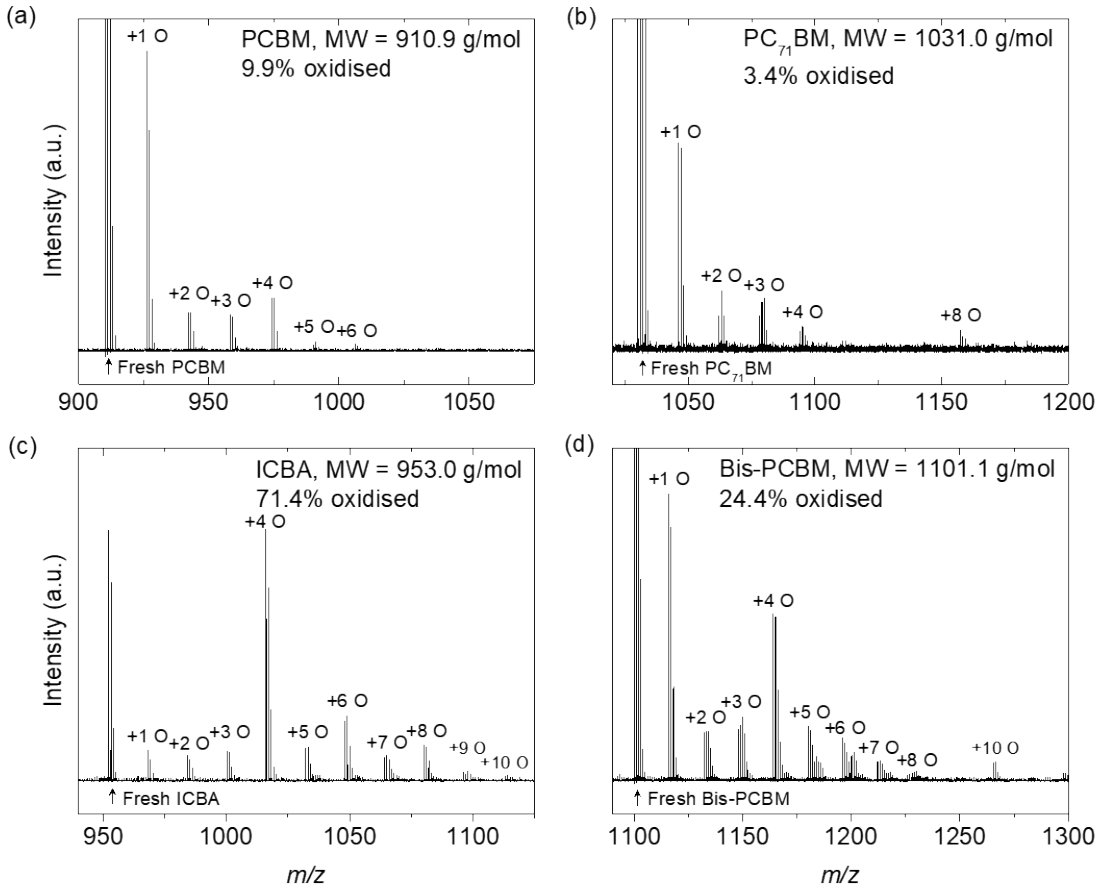
Supplementary Figure 3 UV-visible spectra of PCDTBT:PCBM blend films without and with 60 minutes of exposure to AM1.5G conditions in dry air.



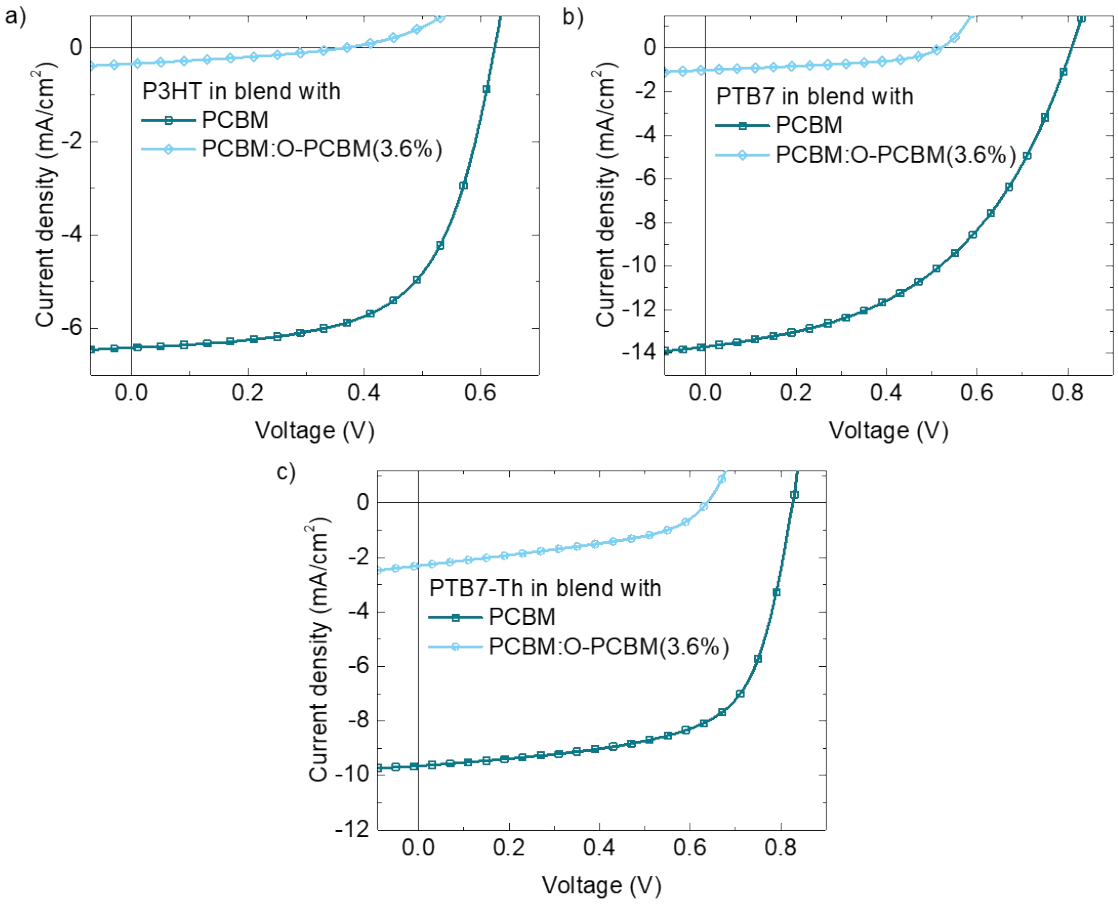
Supplementary Figure 4 AFM height images and average roughness analysis of (a) fresh PCDTBT:PCBM blend films; PCDTBT:PCBM blend films degraded under one sun in dry air for (b) 1 hour and (c) 10 hours; and (d) PCBM degraded in solution under one sun in dry air for 72 hours.



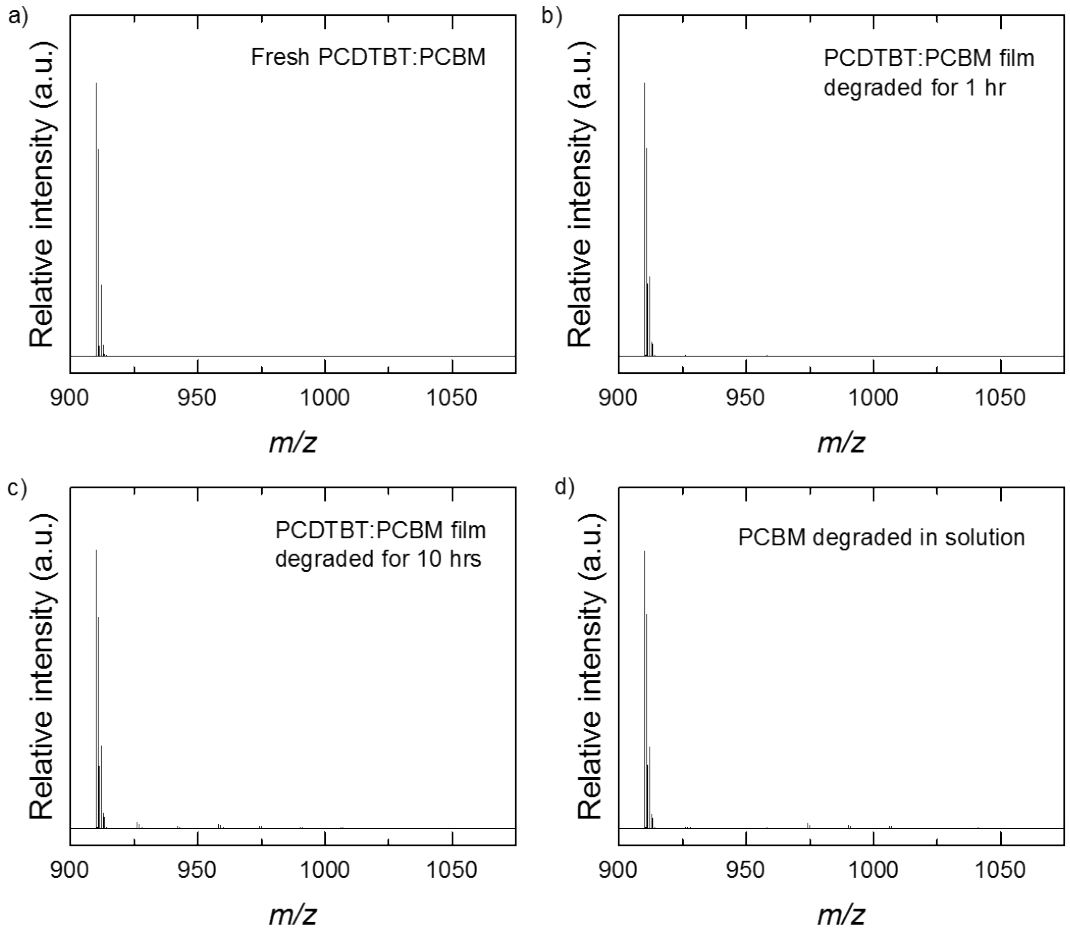
Supplementary Figure 5 (a) XPS O(1s) spectrum of fresh PCDTBT:PCBM blend films with background and O 1s fitting; XPS C(1s), O(1s) and S(2p) spectrum of (b) fresh PCDTBT:PCBM blend films and PCDTBT:PCBM blend films degraded under one sun in dry air for (c) 1 hour and (d) 10 hours; (e) XPS C(1s), O(1s) and S(2p) spectrum of PCDTBT:O-PCBM blend films prepared from selectively degraded PCBM.



Supplementary Figure 6 MALDI-TOF measurement of (a) PCBM; (b) [6,6]-Phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$); (c) indene-C_{60} bis-adduct (ICBA); and (d) Bis(1-[3-(methoxycarbonyl)propyl]-1-phenyl)-[6,6]C_{62} (Bis-PCBM) degraded in films under one sun in air for 32 hours.



Supplementary Figure 7 *J-V* characteristic of devices using different OPV benchmark polymers (a) P3HT, (b) PTB7, and (c) PTB7-Th (also called PCE10) in blend with fresh PCBM and selectively degraded PCBM containing 3.6% of O-PCBM.



Supplementary Figure 8 Full scale MALDI-TOF measurement of (a) fresh PCDTBT:PCBM blend; (b) PCDTBT:PCBM blend film degraded under one sun in air for 1 hour; (c) PCDTBT:PCBM blend film degraded one sun in air for 10 hour; and (d) PCBM degraded in solution under one sun in air. The main peaks at 910.1 in the plots indicate the PCBM molecules.

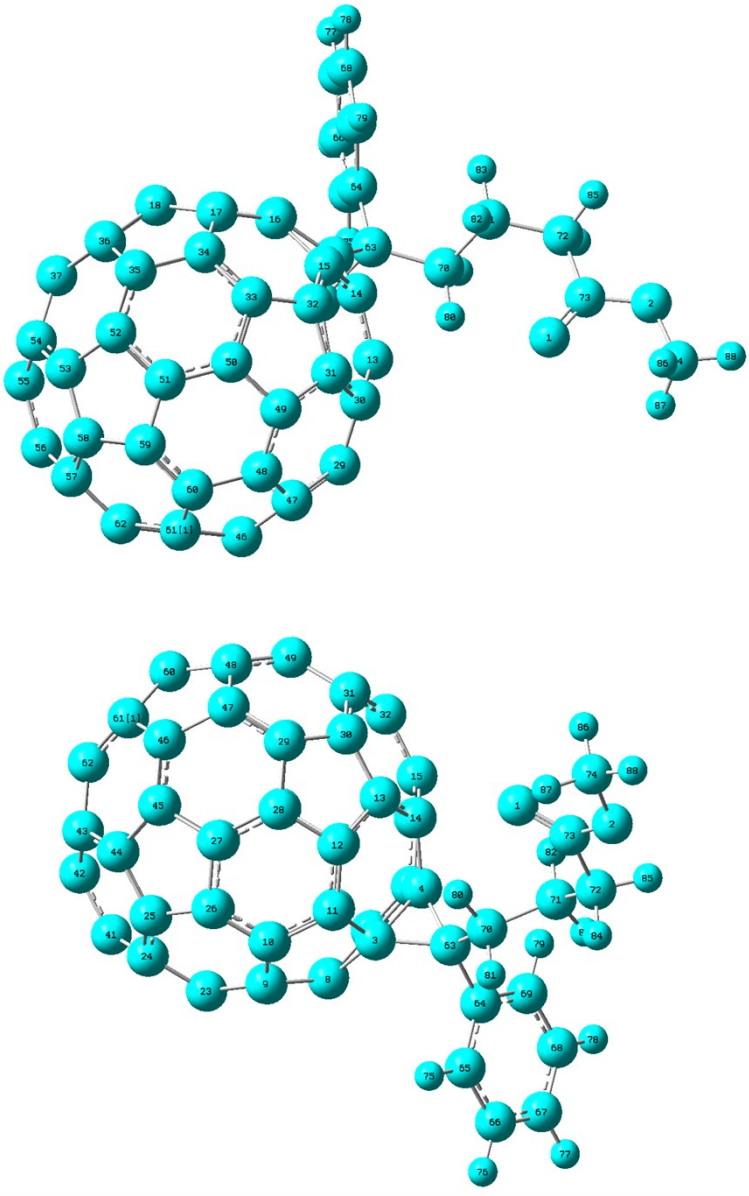
HOMO and LUMO simulations on PCBM with multiple defects

Comparison of HOMO-LUMO simulation methods

The HOMO and LUMO levels were calculated with three different methods: (i) delta SCF (see main text); (ii) taking the Kohn-Sham orbitals; (iii) taking the Kohn-Sham orbital for the HOMO and Kohn-Sham HOMO plus the first excitation energy from TD-DFT for the LUMO. All the calculations are done with Gaussian 09, at the B3LYP level of theory with the 6-31g* basis set. The Kohn-Sham orbitals are obtained from a single point energy calculation on the optimised structure. The TD-DFT calculation yields the excitation energies and the first of these is taken to be added to the Kohn-Sham HOMO energy to obtain the LUMO energy.

The levels were also calculated for PCBM with multiple defects: two epoxide defects, one epoxide and one carbonyl defect, and one epoxide and two carbonyl defects. All defects lower the LUMO level and have a small effect on the HOMO level.

The numbering of the position of a PCBM molecule are shown below:



Supplementary Table 4 Delta-SCF HOMO and LUMO simulations of PCBM and PCBM with different oxygen defects. The values marked in red mean the energy levels go down.

Defect type	Defect position on the PCBM	HOMO from delta-SCF (eV)	Change in HOMO (eV)	HOMO from delta-SCF (eV)	Change in LUMO (eV)
No defect	N/A	-6.72	N/A	-1.83	N/A
One epoxide	11,12	-6.77	-0.05	-2.02	-0.19
	7,8	-6.74	-0.02	-2.03	-0.20
	13,14	-6.76	-0.04	-2.02	-0.19
	5,6	-6.77	-0.05	-2.05	-0.22
	24,25	-6.72	-0.01	-1.81	0.02
	33,34	-6.72	0.00	-1.82	0.01
	55,56	-6.72	0.00	-2.05	-0.22
	16,17	-6.73	-0.01	-2.00	-0.17
	20,38	-6.61	0.11	-1.80	0.03
	29,47	-6.59	0.13	-1.80	0.04
	27,28	-6.59	0.12	-1.83	0.00
	48,49	-6.64	0.08	-1.86	-0.03
	15,32	-6.72	0.00	-2.00	-0.17
	21,22	-6.61	0.11	-1.84	-0.01
	30,31	-6.60	0.12	-1.82	0.01
	10,26	-6.71	0.01	-2.00	-0.17
	39,40	-6.65	0.07	-1.85	-0.02
	9,23	-6.72	0.00	-2.00	-0.17
	45,46	-6.64	0.08	-1.86	-0.03
	36,37	-6.66	0.06	-1.85	-0.02
	57,58	-6.74	-0.02	-2.04	-0.21
	61,62	-6.70	0.02	-2.07	-0.24
	59,60	-6.70	0.02	-2.08	-0.25
	53,54	-6.71	0.01	-2.06	-0.23
	41,42	-6.69	0.02	-1.89	-0.06
	43,44	-6.69	0.02	-1.90	-0.06
	50,51	-6.69	0.03	-1.89	-0.06
	35,52	-6.69	0.03	-1.90	-0.07
	18,19	-6.52	0.20	-1.76	0.07
One Carbonyl	13,14	-6.52	0.20	-2.10	-0.27
	11,12	-6.52	0.20	-2.09	-0.26
	7,8	-6.53	0.19	-2.13	-0.30
	16,17	-6.52	0.20	-2.21	-0.38
	10,26	-6.46	0.26	-2.21	-0.38
	20,38	-6.36	0.35	-2.11	-0.28
	29,47	-6.34	0.38	-2.11	-0.28
	9,23	-6.49	0.22	-2.19	-0.36
	15,32	-6.52	0.20	-2.20	-0.37
	21,22	-6.44	0.28	-2.23	-0.39
	33,34	-6.57	0.15	-2.10	-0.27

	24,25	-6.57	0.15	-2.08	-0.25
	27,28	-6.42	0.30	-2.23	-0.40
	18,19	-6.46	0.26	-2.22	-0.39
	30,31	-6.42	0.30	-2.23	-0.40
	39,40	-6.44	0.28	-2.17	-0.34
	45,46	-6.42	0.30	-2.17	-0.34
	48,49	-6.42	0.30	-2.17	-0.34
	36,37	-6.45	0.27	-2.18	-0.35
	41,42	-6.45	0.27	-2.19	-0.36
	43,44	-6.45	0.27	-2.20	-0.37
	50,51	-6.44	0.28	-2.20	-0.37
	59,60	-6.44	0.28	-2.32	-0.49
	55,56	-6.46	0.26	-2.32	-0.49
	53,54	-6.45	0.28	-2.32	-0.49
	61,62	-6.45	0.27	-2.32	-0.49
	5,6	-6.59	0.13	-2.27	-0.43
	35,52	-6.46	0.26	-2.18	-0.35
	57,58	-6.47	0.25	-2.22	-0.39
Two epoxides	11,12/13,14	-6.68	0.04	-2.25	-0.41
	5,6/7,8	-6.69	0.03	-2.27	-0.44
	11,12/10,26	-6.70	0.02	-2.03	-0.20
	11,12/7,8	-6.74	-0.02	-2.14	-0.31
	5,6/13,14	-6.73	-0.01	-2.16	-0.33
	5,6/20,38	-6.73	-0.01	-2.04	-0.21
Two carbonyls	11,12	-6.74	-0.02	-2.52	-0.69
	20,38	-6.56	0.15	-2.62	-0.79
	29,47	-6.54	0.18	-2.62	-0.79
	16,17	-6.73	-0.01	-2.66	-0.83
	10,26	-6.70	0.02	-2.69	-0.86
	24,25	-6.71	0.01	-2.64	-0.81
	45,46	-6.63	0.09	-2.71	-0.88
	36,37	-6.65	0.07	-2.72	-0.88
	43,44	-6.67	0.05	-2.70	-0.87
	59,60	-6.66	0.06	-2.80	-0.97
	35,52	-6.67	0.05	-2.71	-0.88
	18,19	-6.57	0.15	-2.91	-1.08
	53,54	-6.67	0.05	-2.80	-0.96
	27,28	-6.54	0.18	-2.90	-1.07
	5,6	-6.75	-0.03	-2.67	-0.84
	57,58	-6.69	0.03	-2.74	-0.91
One epoxide and one carbonyl	10,26/24,25	-6.61	0.11	-2.08	-0.25
	10,26/7,8	-6.53	0.19	-2.23	-0.40
	10,26/30,31	-6.43	0.29	-2.39	-0.56
	10,26/20,38	-6.41	0.31	-2.28	-0.45
	10,26/31,30	-6.43	0.29	-2.47	-0.64
	10,26/52,35	-6.40	0.32	-2.34	-0.51
One epoxide	11,12/10,26	-6.76	-0.05	-2.48	-0.65

and two carbonyls	11,12/27,28	-6.79	-0.07	-2.56	-0.73
	11,12/29,47	-6.75	-0.03	-2.65	-0.82
	11,12/43,44	-6.60	0.12	-2.81	-0.98
	11,12/59,60	-6.69	0.03	-2.85	-1.01
	11,12/15,32	-6.72	0.00	-2.81	-0.98
One diol	11,12	-5.65	1.07	-2.13	-0.30
	10,26	-5.93	0.79	-2.41	-0.58
	18,19	-5.99	0.73	-2.15	-0.32
	27,28	-5.97	0.75	-2.13	-0.30
	24,25	-5.78	0.94	-2.21	-0.38
	16,17	-5.86	0.86	-2.76	-0.93
	29,47	-6.11	0.61	-2.69	-0.85
	20,38	-6.13	0.59	-2.69	-0.86
	45,46	-5.88	0.84	-2.38	-0.55
	36,37	-5.89	0.82	-2.38	-0.55
	35,52	-5.93	0.79	-2.37	-0.54
	59,60	-6.07	0.65	-2.60	-0.77
	43,44	-5.99	0.73	-2.67	-0.84
	53,54	-6.23	0.48	-2.78	-0.95
	57,58	-6.03	0.69	-2.45	-0.62
	5,6	-5.80	0.91	-2.36	-0.53

Supplementary Table 5 Kohn-Sham HOMO and LUMO simulations of PCBM and PCBM with different oxygen defects. The values marked in red mean the energy levels go down.

Defect type	Defect position on the PCBM	HOMO from Kohn-Sham (eV)	Change in HOMO (eV)	LUMO from Kohn-Sham LUMO (eV)	Change in LUMO (eV)
No defect	N/A	-5.56	N/A	-3.00	N/A
One epoxide	11,12	-5.62	-0.06	-3.16	-0.16
	7,8	-5.61	-0.05	-3.17	-0.17
	13,14	-5.61	-0.05	-3.16	-0.16
	5,6	-5.64	-0.08	-3.19	-0.19
	24,25	-5.58	-0.02	-2.95	0.05
	33,34	-5.57	-0.01	-2.95	0.05
	55,56	-5.58	-0.02	-3.19	-0.19
	16,17	-5.59	-0.03	-3.13	-0.13
	20,38	-5.48	0.08	-2.94	0.06
	29,47	-5.46	0.10	-2.93	0.07
	27,28	-5.47	0.09	-2.97	0.03
	48,49	-5.50	0.06	-3.00	0.00
	15,32	-5.58	-0.02	-3.13	-0.13
	21,22	-5.48	0.08	-2.98	0.02
	30,31	-5.47	0.09	-2.96	0.04
	10,26	-5.58	-0.02	-3.13	-0.13
	39,40	-5.52	0.04	-2.99	0.01
	9,23	-5.58	-0.02	-3.14	-0.14
	45,46	-5.51	0.05	-3.00	0.00
	36,37	-5.52	0.04	-2.99	0.01
	57,58	-5.57	-0.01	-3.18	-0.18
	61,62	-5.56	0.00	-3.21	-0.21
	59,60	-5.56	0.00	-3.22	-0.22
	53,54	-5.56	0.00	-3.20	-0.20
	41,42	-5.55	0.01	-3.03	-0.03
	43,44	-5.55	0.01	-3.04	-0.04
	50,51	-5.54	0.02	-3.04	-0.04
	35,52	-5.54	0.02	-3.04	-0.04
	18,19	-5.39	0.17	-2.90	0.10
One carbonyl	13,14	-5.39	0.17	-3.21	-0.21
	11,12	-5.39	0.17	-3.21	-0.21
	7,8	-5.39	0.17	-3.25	-0.25
	16,17	-5.38	0.18	-3.33	-0.33
	10,26	-5.33	0.23	-3.34	-0.34
	20,38	-5.24	0.32	-3.27	-0.27
	29,47	-5.22	0.34	-3.26	-0.26
	9,23	-5.38	0.18	-3.33	-0.33
	15,32	-5.41	0.15	-3.34	-0.34
	21,22	-5.33	0.23	-3.34	-0.34
	33,34	-5.44	0.12	-3.24	-0.24

	24,25	-5.44	0.12	-3.22	-0.22
	27,28	-5.31	0.25	-3.34	-0.34
	18,19	-5.34	0.22	-3.34	-0.34
	30,31	-5.31	0.25	-3.34	-0.34
	39,40	-5.32	0.24	-3.32	-0.32
	45,46	-5.30	0.26	-3.32	-0.32
	48,49	-5.30	0.26	-3.32	-0.32
	36,37	-5.32	0.24	-3.33	-0.33
	41,42	-5.31	0.25	-3.35	-0.35
	43,44	-5.31	0.25	-3.35	-0.35
	50,51	-5.31	0.25	-3.35	-0.35
	59,60	-5.30	0.26	-3.46	-0.46
	55,56	-5.32	0.24	-3.46	-0.46
	53,54	-5.31	0.25	-3.46	-0.46
	61,62	-5.31	0.25	-3.47	-0.47
	5,6	-5.46	0.10	-3.37	-0.37
	35,52	-5.32	0.24	-3.33	-0.33
	57,58	-5.33	0.23	-3.37	-0.37
Two epoxides	11,12/13,14	-5.54	0.02	-3.38	-0.38
	5,6/7,8	-5.56	0.00	-3.40	-0.40
	11,12/10,26	-5.56	0.00	-3.17	-0.17
	11,12/7,8	-5.60	-0.04	-3.28	-0.28
	5,6/13,14	-5.60	-0.04	-3.29	-0.29
	5,6/20,38	-5.60	-0.04	-3.16	-0.16
One epoxide, one carbonyl	10,26/24,25	-5.48	0.08	-3.23	-0.23
	10,26/7,8	-5.40	0.16	-3.35	-0.35
	10,26/30,31	-5.33	0.23	-3.50	-0.50
	10,26/20,38	-5.29	0.27	-3.43	-0.43
	10,26/31,30	-5.33	0.23	-3.59	-0.59
	10,26/52,35	-5.27	0.29	-3.50	-0.50
One epoxide, two carbonyls	11,12/10,26	-5.63	-0.07	-3.61	-0.61
	11,12/27,28	-5.67	-0.11	-3.71	-0.71
	11,12/29,47	-5.62	-0.06	-3.80	-0.80
	11,12/43,44	-5.48	0.08	-3.96	-0.96
	11,12/59,60	-5.56	0.00	-4.00	-1.00
	11,12/15,32	-5.59	-0.03	-3.94	-0.94
Two Carbonyls	11,12	-5.61	-0.05	-3.64	-0.64
	20,38	-5.45	0.11	-3.78	-0.78
	29,47	-5.42	0.14	-3.77	-0.77
	16,17	-5.60	-0.04	-3.80	-0.80
	10,26	-5.58	-0.02	-3.83	-0.83
	24,25	-5.58	-0.02	-3.79	-0.79
	45,46	-5.51	0.05	-3.86	-0.86
	36,37	-5.53	0.03	-3.87	-0.87
	43,44	-5.54	0.02	-3.87	-0.87
	59,60	-5.53	0.03	-3.96	-0.96
	35,52	-5.54	0.02	-3.87	-0.87

	18,19	-5.47	0.09	-4.06	-1.06
	53,54	-5.53	0.03	-3.95	-0.95
	27,28	-5.43	0.13	-4.05	-1.05
	5,6	-5.67	-0.11	-3.78	-0.78
	57,58	-5.55	0.01	-3.91	-0.91
Diol	11,12	-4.67	0.89	-3.00	0.00
	10,26	-4.90	0.66	-3.33	-0.33
	18,19	-5.00	0.56	-3.06	-0.06
	27,28	-4.98	0.58	-3.04	-0.04
	24,25	-4.80	0.76	-3.10	-0.10
	16,17	-5.07	0.49	-3.61	-0.61
	29,47	-4.99	0.57	-3.61	-0.61
	20,38	-5.02	0.54	-3.63	-0.63
	45,46	-4.89	0.67	-3.27	-0.27
	36,37	-4.90	0.66	-3.27	-0.27
	35,52	-4.91	0.65	-3.31	-0.31
	59,60	-5.09	0.47	-3.47	-0.47
	43,44	-5.11	0.45	-3.58	-0.58
	53,54	-5.16	0.40	-3.68	-0.68
	57,58	-5.05	0.51	-3.35	-0.35
	5,6	-4.85	0.71	-3.23	-0.23

Supplementary Table 6 Kohn-Sham HOMO and TD-DFT LUMO simulations of PCBM and PCBM with different oxygen defects. The values marked in red mean the energy levels go down.

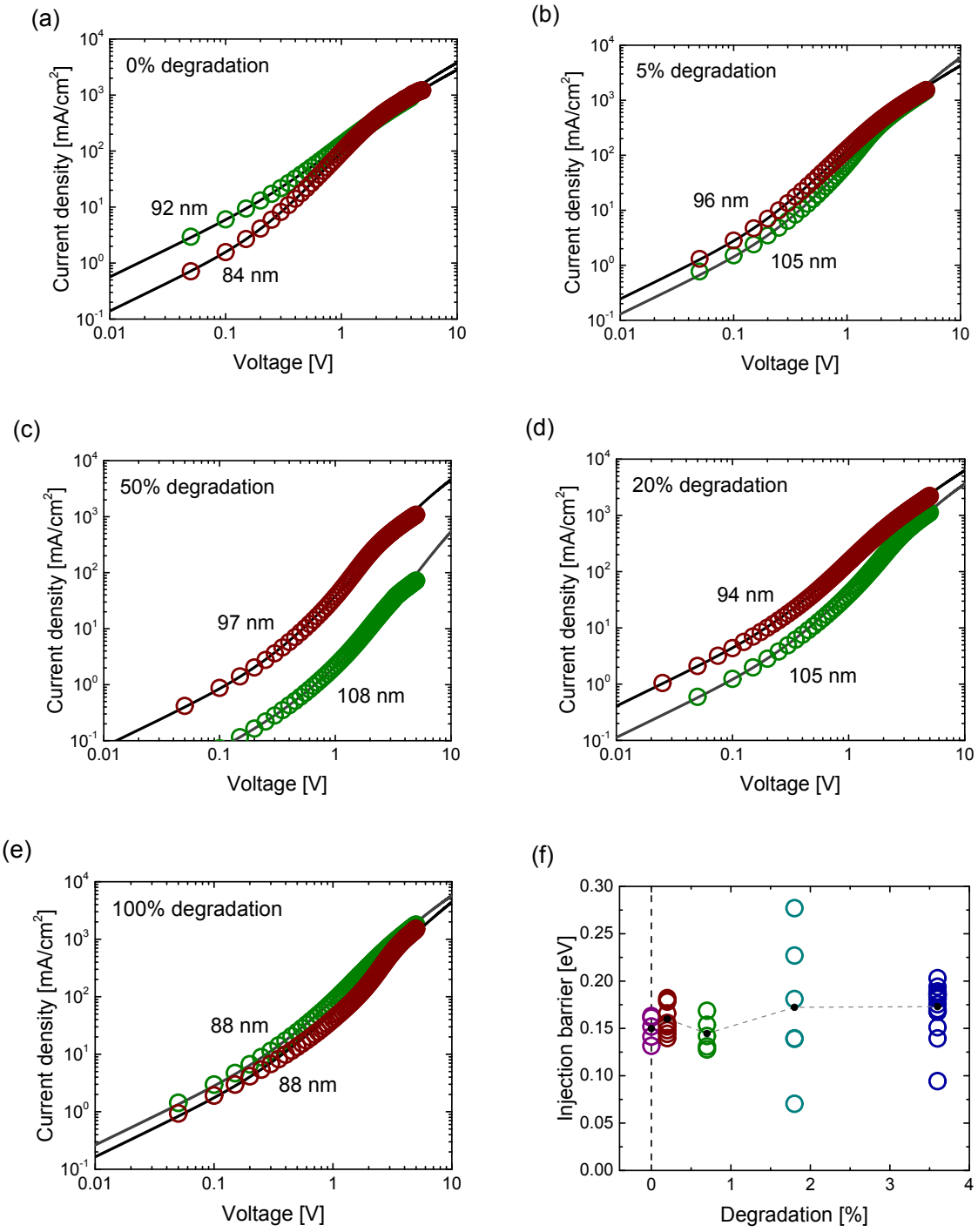
Defect type	Defect position on the PCBM	Kohn-Sham HOMO (eV)	Change in HOMO (eV)	1st excited state energy (eV)	TD-DFT LUMO (eV)	Change in LUMO (eV)
No defect	N/A	-5.56	N/A	1.93	-3.63	N/A
One epoxide	11,12	-5.62	-0.06	1.85	-3.77	-0.14
	7,8	-5.61	-0.05	1.84	-3.77	-0.14
	13,14	-5.61	-0.05	1.84	-3.77	-0.14
	5,6	-5.64	-0.07	1.85	-3.79	-0.15
	24,25	-5.58	-0.02	2.03	-3.55	0.08
	33,34	-5.57	-0.01	2.02	-3.55	0.08
	55,56	-5.58	-0.02	1.78	-3.80	-0.17
	16,17	-5.59	-0.03	1.84	-3.75	-0.12
	20,38	-5.48	0.08	1.93	-3.55	0.08
	29,47	-5.46	0.10	1.92	-3.53	0.10
	27,28	-5.47	0.10	1.89	-3.58	0.05
	48,49	-5.50	0.06	1.90	-3.61	0.03
	15,32	-5.58	-0.02	1.83	-3.75	-0.12
	21,22	-5.48	0.08	1.89	-3.59	0.04
	30,31	-5.47	0.09	1.90	-3.57	0.06
	10,26	-5.58	-0.01	1.82	-3.75	-0.12
	39,40	-5.52	0.05	1.93	-3.59	0.04
	9,23	-5.58	-0.02	1.83	-3.75	-0.12
	45,46	-5.51	0.05	1.90	-3.60	0.03
	36,37	-5.52	0.04	1.93	-3.59	0.04
	57,58	-5.57	-0.01	1.77	-3.80	-0.17
	61,62	-5.56	0.00	1.74	-3.82	-0.19
	59,60	-5.56	0.01	1.73	-3.82	-0.19
	53,54	-5.56	0.00	1.75	-3.81	-0.18
	41,42	-5.55	0.02	1.90	-3.65	-0.02
	43,44	-5.55	0.01	1.89	-3.65	-0.02
	50,51	-5.54	0.02	1.89	-3.65	-0.02
	35,52	-5.54	0.02	1.89	-3.65	-0.02
	18,19	-5.39	0.17	1.87	-3.51	0.12
Two Carbonyls	11,12	-5.61	-0.05	1.39	-4.22	-0.59
	20,38	-5.45	0.12	1.03	-4.42	-0.79
	29,47	-5.42	0.14	1.01	-4.41	-0.78
	16,17	-5.60	-0.04	0.97	-4.63	-1.00
	10,26	-5.58	-0.02	0.99	-4.59	-0.96
	24,25	-5.58	-0.02	1.11	-4.48	-0.85
	45,46	-5.51	0.05	1.05	-4.46	-0.82
	36,37	-5.53	0.03	1.04	-4.49	-0.86
	43,44	-5.54	0.02	1.05	-4.49	-0.86
	59,60	-5.53	0.03	1.12	-4.41	-0.78
	35,52	-5.54	0.03	1.04	-4.49	-0.86

	18,19	-5.47	0.10	0.73	-4.74	-1.11
	53,54	-5.53	0.03	1.01	-4.53	-0.89
	27,28	-5.43	0.13	0.70	-4.74	-1.10
	5,6	-5.67	-0.11	1.07	-4.60	-0.97
	57,58	-5.55	0.01	1.28	-4.27	-0.64
Diol	11,12	-4.67	0.90	1.36	-3.31	0.32
	10,26	-4.90	0.66	1.11	-3.79	-0.16
	18,19	-5.00	0.56	1.47	-3.52	0.11
	27,28	-4.98	0.58	1.46	-3.52	0.11
	24,25	-4.80	0.77	1.47	-3.33	0.30
	16,17	-5.07	0.49	0.84	-4.23	-0.60
	29,47	-4.99	0.57	1.46	-3.53	0.10
	20,38	-5.02	0.54	0.73	-4.29	-0.66
	45,46	-4.89	0.67	1.21	-3.68	-0.05
	36,37	-4.90	0.66	1.20	-3.70	-0.07
	35,52	-4.91	0.65	0.71	-4.21	-0.58
	59,60	-5.09	0.48	1.06	-4.02	-0.39
	43,44	-5.11	0.45	0.88	-4.24	-0.60
	53,54	-5.16	0.40	0.92	-4.24	-0.61
	57,58	-5.05	0.51	1.16	-3.89	-0.26
	5,6	-4.85	0.72	1.37	-3.47	0.16

Supplementary Table 7 Change in HOMO and LUMO levels base on the Boltzmann average. The values marked in red mean the energy levels go down.

Defect type	Change in HOMO (delta-SCF)	Change in LUMO (delta-SCF)	Change in HOMO (Kohn-Sham)	Change in LUMO (Kohn-Sham)	Change in LUMO (TD-DFT)
One epoxide	0.04	-0.10	0.02	-0.07	-0.05
One carbonyl	0.25	-0.36	0.22	-0.33	-0.31
Two epoxides	0.01	-0.32	-0.01	-0.29	-0.29
One epoxide, one carbonyl	0.25	-0.47	0.21	-0.43	-0.43
One epoxide, two carbonyls	0.00	-0.86	-0.03	-0.84	-0.81
Two carbonyls	0.06	-0.88	0.03	-0.87	-0.87
Diol	0.77	-0.62	0.60	-0.60	-0.58

Space charge limited current analysis



Supplementary Figure 9 (a-e) SCLC current density-voltage data for PCBM electron-only devices with increasing concentrations of O-PCBM. Experimental curves are presented with open circles and the drift-diffusion fits with solid lines. **(f)** Values of the barrier for electron injection into electron only devices containing different fractions of O-PCBM, obtained from the fitting procedure described in the text.

Solar cell *J–V* curve simulations

Both the dark and illuminated solar cell *J-V* curves were simulated using a commercially available drift-diffusion solver called *Advanced Semiconductor Analysis* (ASA) [https://www.cambridge.org/core/journals/journal-of-materials-research/article/optical-and-electrical-modeling-of-thinfilm-silicon-solar-cells/BF97415DB87ACB26ACD99B9FBB32C7B6]. For the illuminated devices, a constant generation rate was chosen to match the current density of the experimental curves when a band gap of 1.4 eV was used. With the presence of a deep Gaussian electron trap level, recombination of trapped electrons and free holes was used along with direct band-to-band recombination. The choice of electron band mobility, Gaussian trap level and Gaussian density was chosen based on the mean values of the SCLC fitting results. All fixed values and varied values are shown in the table below.

Quantity	Value	Units
Fixed values		
Band gap	variable	eV
Effective electron density	10^{19}	cm^{-3}
Effective hole density	10^{19}	cm^{-3}
Dielectric constant	3	-
Active layer thickness	70	nm
Electron band mobility	variable	cm^2/Vs
Hole band mobility	$3 \cdot 10^{-3}$	cm^2/Vs
Injection barrier (electrons)	variable	eV
Injection barrier (holes)	0.2	eV
Gaussian density	variable	cm^{-3}
Gaussian level	variable	eV
Gaussian standard deviation	0.1	eV
Surface recomb. velocity	10^5	m/s
Electron capture rate (neut.)	10^{-10}	$cm^{-3}\,s^{-1}$
Electron capture rate (pos.)	10^{-10}	$cm^{-3}\,s^{-1}$
Hole capture rate (neut.)	10^{-10}	$cm^{-3}\,s^{-1}$
Hole capture rate (neg.)	10^{-10}	$cm^{-3}\,s^{-1}$
Generation rate	$7.7 \cdot 10^{21}$	$cm^{-3}\,s^{-1}$
Direct recombination rate	$7.7 \cdot 10^{-19}$	$cm^{-3}\,s^{-1}$
Series resistance	$3.07 \cdot 10^{-4}$	Ωm^2
Shunt resistance	0.29	Ωm^2
0% O-PCBM device		
Band gap	1.398	eV
Injection barrier	0.2	eV
Electron band mobility	$8.2 \cdot 10^{-4}$	cm^2/Vs
Gaussian density	$2.4 \cdot 10^{16}$	cm^{-3}
Gaussian level	-0.2073	eV
1.8% O-PCBM device		
Band gap	1.363	eV
Injection barrier	0.165	eV
Electron band mobility	$8.8 \cdot 10^{-4}$	cm^2/Vs
Gaussian density	$1.6 \cdot 10^{17}$	cm^{-3}
Gaussian level	-0.1723	eV
3.6% O-PCBM device		
Band gap	1.277	eV
Injection barrier	0.0785	eV
Electron band mobility	$6.3 \cdot 10^{-5}$	cm^2/Vs
Gaussian density	$6.8 \cdot 10^{17}$	cm^{-3}
Gaussian level	-0.086	eV

Charge extraction simulations

The excess charge-carrier density obtained from charge extraction (CE) measurements were simulated by subtracting the total charge-carrier density at V_{oc} under varying illumination by the total charge-carrier density at V = 0 V in the dark. The total charge-carrier density is here the sum of the average values of the electrons densities, hole densities, trap densities and surface charge densities (assuming that enough time has passed that all trapped charge carriers have thermally escaped and are extracted at the contacts).

V_{OC} reconstruction from charge extraction (CE) and transient photovoltage (TPV) measurements

The charge density VS V_{OC} data from CE was fitted with the exponential function:

$$n = n_0 exp\left(\frac{qV_{OC}}{mkT}\right)$$

The lifetime VS V_{OC} data from TPV was fitted with the exponential function:

$$\tau_{\Delta n} = \tau_{\Delta n0} exp\left(-\frac{qV_{OC}}{\vartheta kT}\right)$$

The lifetime of the charge generated by the TPV pulse, $\tau_{\Delta n}$, can be related to the lifetime of the total charge *n* by the relationship:

$$\tau_n = \delta\tau_{\Delta n}$$

Where:

$$\delta = \frac{m}{\vartheta} + 1$$

Therefore:

$$\tau_n = \delta\tau_{\Delta n0} exp\left(-\frac{qV_{OC}}{\vartheta kT}\right)$$

At open circuit, the generation and recombination currents are equal:

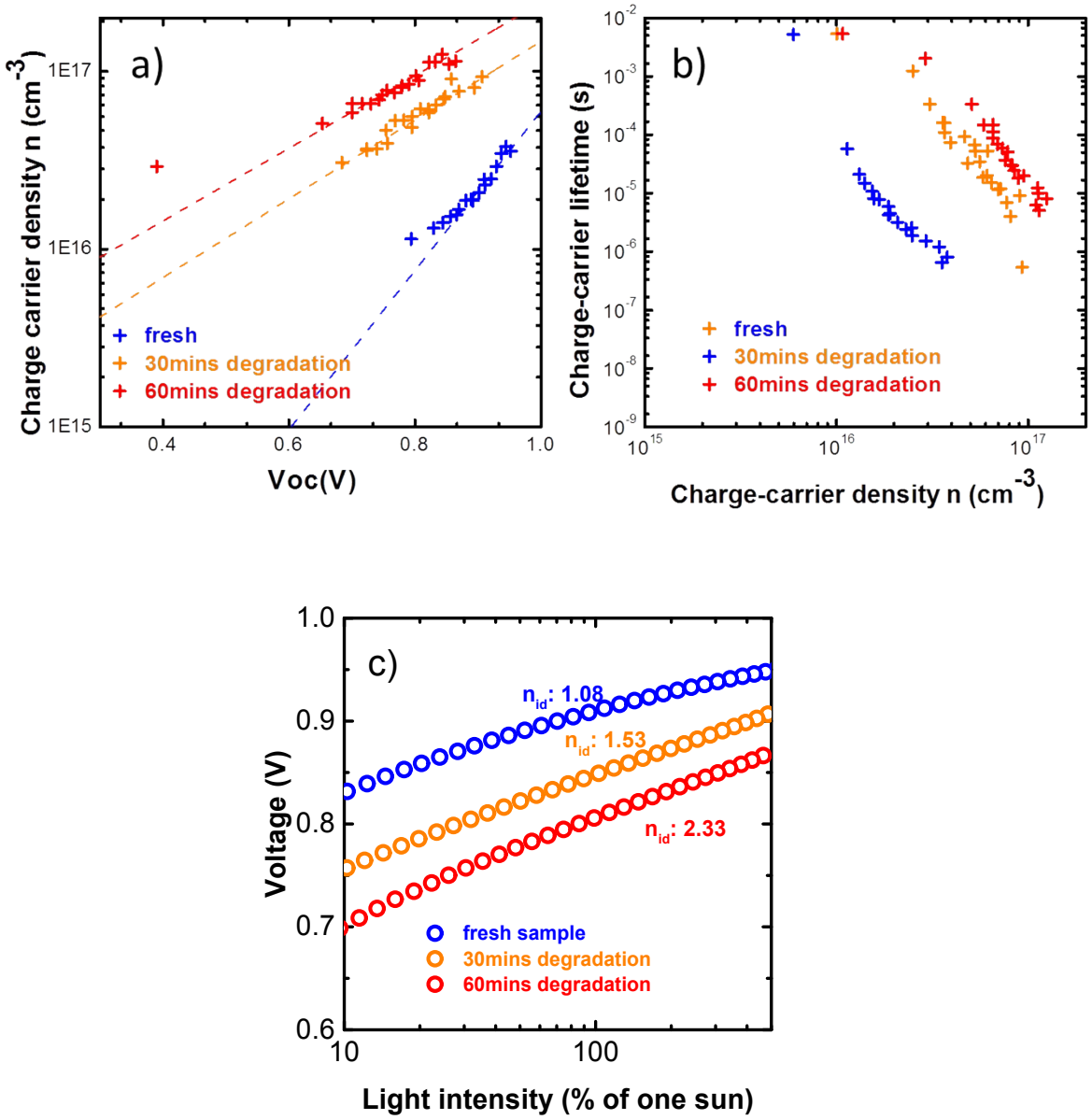
$$J_{gen} \approx J_{SC} = J_{loss} = qd\frac{n}{\tau_n} = qd\frac{n_0 exp\left(\frac{qV_{OC}}{mkT}\right)}{\delta\tau_{\Delta n0} exp\left(-\frac{qV_{OC}}{\vartheta kT}\right)}$$

$$\frac{\delta J_{SC}\tau_{\Delta n0}}{qdn_0} = \frac{exp\left(\frac{qV_{OC}}{mkT}\right)}{exp\left(-\frac{qV_{OC}}{\vartheta kT}\right)}$$

$$ln\left(\frac{\delta J_{SC}\tau_{\Delta n0}}{qdn_0}\right)=\frac{qV_{OC}}{kT}\left(\frac{1}{m}+\frac{1}{\vartheta}\right)$$

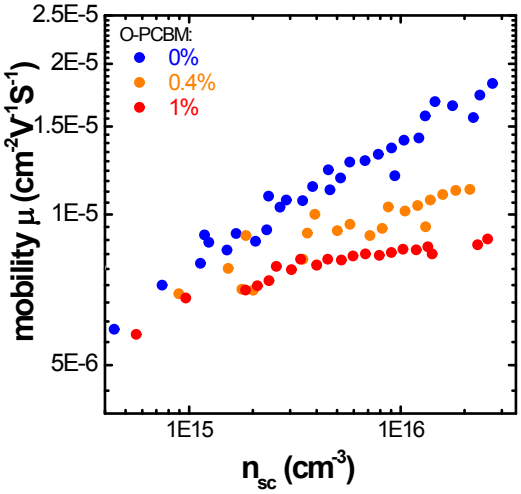
$$V_{OC}\left(\frac{1}{m}+\frac{1}{\vartheta}\right)=\frac{kT}{q}ln\left(\frac{\delta J_{SC}\tau_{\Delta n0}}{qdn_0}\right)$$

$$V_{OC}=\frac{mkT}{q\delta}ln\left(\frac{\delta J_{SC}\tau_{\Delta n0}}{qdn_0}\right)$$

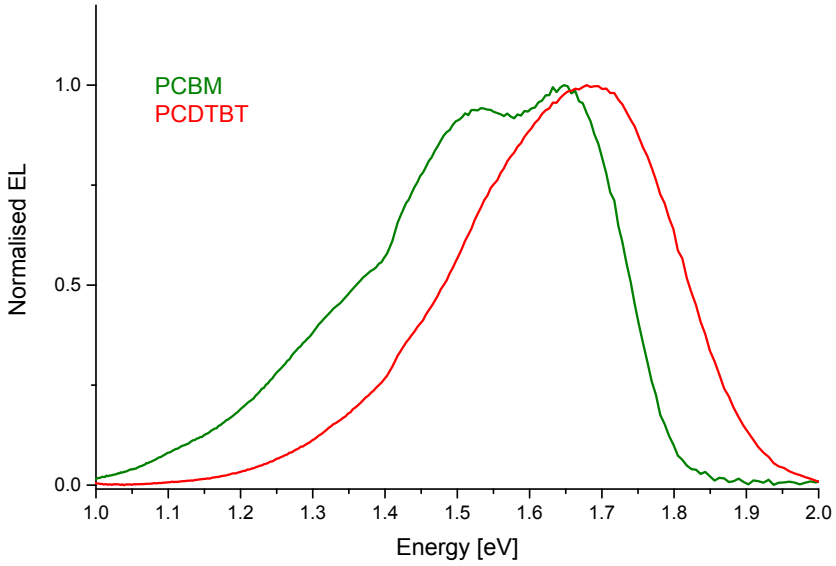


Supplementary Figure 10 CE, TPV, and diode ideality analysis of PCDTBT:PCBM blend devices prepared from blends degraded as films under AM1.5G illumination in dry air for 30 minutes and 60 minutes prior to electrode deposition. (a) Charge-carrier density *n* as a function of V_{oc} as measured from CE (produced by varying the illumination intensity), the dashed line corresponds to mono-

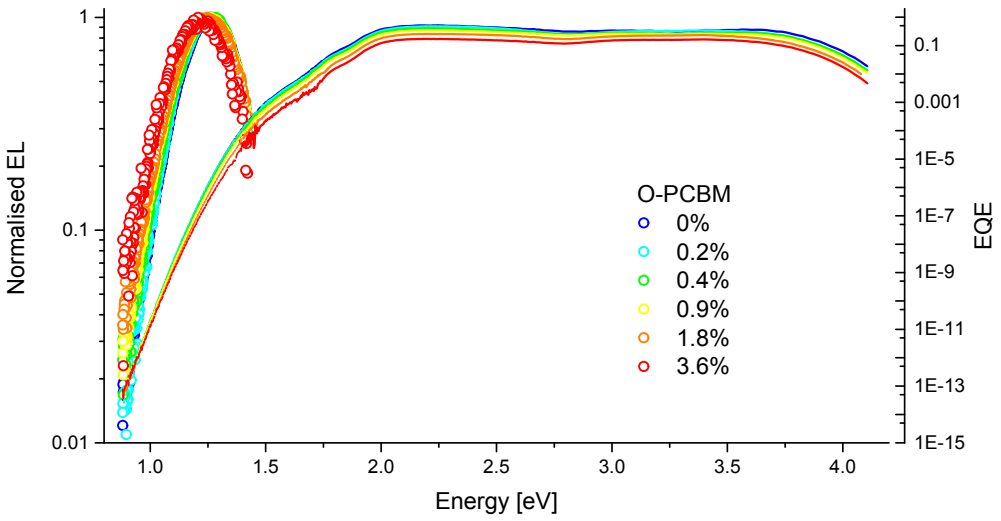
exponential fit; (b) charge-carrier lifetimes at varying charge-carrier density as measured from TPV; (c) Measured V_{OC} (open circles) at varying illumination intensities.



Supplementary Figure 11 Effective mobility measured by charge extraction at short circuit as a function of carrier density for PCDTBT:PCBM blend devices with increasing fraction of O-PCBM.



Supplementary Figure 12 Normalised electroluminescence spectra of devices containing only pure PCBM or only pure PCDTBT. Both emissions occur at higher energies than the charge transfer emission recorded in devices containing PCDTBT:PCBM blends.



Supplementary Figure 13 Normalised electroluminescence (EL) and absolute external quantum efficiency (EQE) spectra of PCDTBT:PCBM devices containing increasing amounts of photo-oxidised PCBM (O-PCBM). The quantum efficiency data that could be directly collected on our EQE instrument is represented by solid lines (down to about 1.5 eV), while the EQE data below 1.5 eV was obtained from the EL data, after dividing by the black body photon flux and multiplying by a pre-factor to match with the absolute EQE data.

Detailed balance method to calculate voltage losses

The maximum voltage achievable in a solar cell is limited by unavoidable radiative recombination. In the radiative limit, where absorption and emission quantum efficiencies are equal, the maximum voltage achievable can be related to the electroluminescence quantum efficiency (Q_{LED}).

The Q_{LED} is a function of the electroluminescence photo flux and the injection current density:

From the ideal diode equation, we can deduce the open circuit voltage in the radiative limit at open circuit (ideality factor = 1, only radiative recombination):

$$V_{OC,rad} = \frac{kT}{q} ln\left(\frac{J_{SC}(V_{OC,rad})}{J_{0,rad}} + 1\right)$$

Assuming no losses at short circuit (SC):

$$J_{SC}(V_{OC,rad}) \approx J_{SC}$$

The saturation current in the radiative limit can be calculated from the electroluminescence quantum efficiency (Q_{EL}).

$$J_{0,rad} = q \int Q_{EL}(E) \phi_{BB}(E) dE$$

As our electroluminescence system could not measure an absolute value of electroluminescence photon flux, Q_{EL} was obtained by matching the EL data to the calibrated EQE data, by multiplying them by a pre-factor.

Supplementary Table 8 Voltage values calculated for PCDTBT:PCBM devices with increasing fractions of photo-oxidised PCBM (O-PCBM). $V_{OC,SQ}$: Schokley-Queisser limit to V_{OC}; $V_{OC,rad}$: radiative limit to V_{OC}, measured using EQE-EL; V_{OC}: measured using a solar simulator; $\Delta V_{OC,abs}$: voltage losses due to non-ideal absorption (EQE < 1 above the band gap energy and sloped absorption edge); $\Delta V_{OC,non\text{-}rad}$: voltage losses due to non-radiative recombination only.

O-PCBM [%]	$V_{OC,SQ}$ [V]	$V_{OC,rad}$ [V]	V_{OC} [V]	$\Delta V_{OC,abs}$ [V]	$\Delta V_{OC,non\text{-}rad}$ [V]
0	1.545	1.246	0.923	0.299	0.323
0.2	1.545	1.240	0.882	0.305	0.358
0.4	1.545	1.241	0.846	0.303	0.396
0.9	1.545	1.224	0.775	0.321	0.449
1.8	1.555	1.234	0.731	0.320	0.503
3.6	1.555	1.229	0.614	0.326	0.616