Supplementary Information:

Toward Improved Environmental Stability of Polymer:Fullerene and Polymer:Nonfullerene Organic Solar Cells: A Common Energetic Origin of Light and Oxygen Induced Degradation

Emily M. Speller^{*a*}, Andrew J. Clarke^{*a*}, Nicholas Aristidou^{*b*}, Mark F. Wyatt^{*c*}, Laia Francàs ^{*b*}, George Fish^{*b*}, Hyojung Cha^{*b*}, Harrison Ka Hin Lee^{*a*}, Joel Luke^{*d*}, Andrew Wadsworth ^{*b*}, Alex D. Evans^{fg}, Iain McCulloch^{*be*}, Ji-Seon Kim^{*d*}, Saif A. Haque^{*b*}, James R. Durrant^{*ab*}, Stoichko D. Dimitrov^{*a*}, Wing C. Tsoi^{**a*}, Zhe Li^{* f}

^a SPECIFIC, College of Engineering, Swansea University, Bay Campus, Fabian Way, Swansea SA1 8EN, United Kingdom, *Email: <u>w.c.tsoi@swansea.ac.uk</u>

^b Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, United Kingdom

^c EPSRC UK National Mass Spectrometry Facility (NMSF), Swansea University Medical School, Wales SA2 8PP, United Kingdom

^{*d*} Department of Physics and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, United Kingdom

^e Physical Sciences and Engineering Division, KAUST Solar Center (KSC), King Abdullah University of Science and Technology (KAUST), KSC Thuwal 23955-6900, Saudi Arabia ^f School of Engineering, Cardiff University, Newport Road, Cardiff, CF24 3AA, United Kingdom *Email: <u>liz75@cardiff.ac.uk</u>

^g School of Physics and Astronomy, Cardiff University, Newport Road, Cardiff, CF24 3AA, United Kingdom

Experimental Methods

Materials: Regio-regular P3HT was purchased from Rieke Metals (mw = 53K or 69 K g/mol for use with nfas and fullerenes respectively) and PCBM, PC₇₁BM, Bis-PCBM, ICBA, ICTA and Kloc-6 were purchased from Solenne BV. All non-fullerene acceptors were chemically synthesised in house. PCDTBT (mw = 50-60K g/mol) and PBDB-T (PCE12) (mw = 80-100K g/mol) were purchased from 1-Material.

Film preparation: All substrates were cleaned by sonication in acetone and isopropanol, followed by a plasma treatment. Quartz substrates were used for UV-vis and transient absorption measurements. 1 x 1 cm² glass substrates were used for fluorescence spectroscopy measurements. 1 x 2 cm² indium tin oxide substrates were used for cyclic voltammetry measurements. Solutions were prepared by dissolving P3HT:NFA (10:10 mg/ml) and P3HT:FA (24:24 mg/ml) in chlorobenzene and were mixed overnight on a hotplate at 60°C. Films were spincoated with a thickness of ~40 nm for P3HT:IDFBR and ~100 nm for all other films to match those employed in optimised devices. All films were annealed on a hotplate in a nitrogen environment at 130°C for 10 minutes.

Photochemical degradation: Photo-aging of the films/devices was performed under \sim 1 Sun AM1.5G in ambient conditions and temperature using a solar simulator, with no filters, for the aging time specified in the text.

UV–visible absorption: The UV–vis absorbance spectra were measured with a Perkin Elmer Lambda 750 spectrophotometer (PerkinElmer, Seer Green, UK), using a quartz substrate as a reference sample for calibration.

Microsecond transient absorption: Microsecond transient absorption kinetics were measured using laser excitation pulses (<10 ns) generated from a tuneable optical parametric oscillator (Opolette 355). Samples were probed using the light output of a tungsten lamp and signals were recorded with Si and InGaAs photodiodes, housed in a preamplifier and an electronic filter (Costronics Electronics) connected to a dual channel oscilloscope and PC. Probe wavelengths were selected with a monochromator. The films were kept under a nitrogen atmosphere to prevent film degradation.

Superoxide probe measurements: A stock 31.7μ M solution of the hydroethidine probe was prepared by dissolving 10 mg in 10 ml of dry toluene; sonication was used to facilitate miscibility. Films were then added to 10 ml of 0.317μ M solution created from the stock solution. Photoluminescence spectra were recorded using an excitation wavelength of 520 nm and slit widths of 10 mm on a Horiba Yobin-Ybon Fluorolog-3 spectrofluorometer. Films were sealed in a controlled environment, where dry air was gassed through for the duration of the degradation and illumination was provided by a tungsten lamp equipped with a UV-blocking filter as previously reported.

Cyclic voltammetry: Cyclic voltammetry measurements were performed using a Ag/AgCl reference electrode (standardised against Ferrocene/Ferrocenium), a platinum gauze wrapped around a platinum wire as the counter electrode and the thin film sample on ITO as the working electrode all submerged in 0.1 M of tetrabutylammonium 3 hexauorophosphate (TBAHFP) in anhydrous acetonitrile electrolyte that was degassed with dry nitrogen. The potential difference between counter and working electrodes was controlled by a potentiostat from Metrohm Autolab.

Photoluminescence spectroscopy: A Renishaw inVia Raman Microscope with 532 nm excitation laser were used to obtain PL spectra of full devices. A 2 x 4.2 mm map was measured over each pixel with 242 spectra per map. At least 4 pixels were measured and averaged for each degradation condition.

Atomic Force Microscopy: A Dimension 3100 system was used for Atomic Force Microscopy (AFM), with a Bruker tip model MLCT, with nominal resonant frequencies in the range 7-15KHz in tapping mode. RMS roughness is calculated using the standard method, equation:

$$Rrms = \sqrt{\frac{1}{n} * \sum x^2}$$

where x is the height at a measured point and n is the number of points. All post processing and analysis is done with the Gwyddion SPM analysis software.

Mass spectrometry: Samples for mass spectrometry were prepared by redissolving films in chlorobenzene at an approximate concentration of 1 mg mL⁻¹. MALDI matrix anthracene (Sigma-Aldrich Company Ltd., Gillingham, UK) was dissolved in chlorobenzene at 10 mg mL⁻¹. Solutions of sample and matrix were mixed together so the matrix was in ~250–1000 fold molar excess, typically 1 µL of sample to 49 µL of matrix. 0.5 µL of each of these mixture solutions for each sample was spotted onto the MALDI plate and dried in air. MALDI-TOF spectra were acquired in negative-reflectron mode using an ultrafleXtreme mass spectrometer (Bruker Daltonics, Bremen, Germany), which is equipped with a Smartbeam-II Nd:YAG laser (λ = 355 nm); sample ions were observed as negative radical species (M^{-•}). Data was acquired using flexControl software v3.4, while ost-acquisition processing of data was performed by flexAnalysis software v3.4.



Figure S1 Chemical structures and full chemical names of the materials investigated.

Photoaging Time (mins)	PCE (%)	J _{sc} (mAcm ⁻²)	V _{oc} (V)	FF
0	5.61	11.3	0.75	0.66
5	1.17	4.14	0.59	0.48
10	0.73	3.18	0.49	0.46
30	0.28	1.96	0.33	0.44

Table S1 Device characteristics for ITO/ZnO/P3HT:O-IDTBR/MoO₃/Ag devices with different photo-aging times prior to electrode deposition under simulated AM 1.5G illumination in dry air.

Photoaging Time (mins)	PCE (%)	J _{sc} (mAcm ⁻²)	V _{oc} (V)	FF
0	3.17	7.64	0.58	0.57
10	2.75	8.09	0.54	0.50
30	2.19	6.91	0.51	0.49

Table S2 Device characteristics for ITO/ZnO/P3HT:PCBM/MoO₃/Ag devices with different photo-aging times prior to electrode deposition under simulated AM 1.5G illumination in dry air.



Figure S2 Current density-voltage (J-V) characteristics of OSCs with a structure of ITO/ZnO/P3HT:O-IDTBR/MoO₃/Ag devices degraded under different conditions (AM1.5G illumination in nitrogen (N_2), AM1.5G illumination in air, and dark storage in air) prior to electrode deposition.

	PCE (%)	J _{sc} (mAcm ⁻²)	V _{oc} (V)	FF
Fresh	3.83	9.19	0.71	0.59
10 mins AM1.5G & N_2	3.82	9.01	0.70	0.60
10 mins AM1.5G & air	1.94	5.13	0.69	0.55
10 mins dark & air	3.87	8.95	0.72	0.60

Table S3 Device characteristics for ITO/ZnO/P3HT:O-IDTBR/MoO₃/Ag devices degraded with different conditions (AM1.5G illumination in nitrogen (N_2), AM1.5G illumination in air, and dark storage in air) prior to electrode deposition.



Figure S3 UV-visible absorbance spectra of P3HT:O-IDTBR thin films photo-aged a) under AM1.5G illumination in nitrogen and b) in the dark in air for up to 8 hours.



Figure S4 Photoluminescence spectra (excited at 532 nm) of devices aged prior to electrode deposition under different conditions: AM1.5G illumination in air; AM1.5G illumination in nitrogen (N_2); and dark storage in air. The reduction of PL intensity due to exposure under AM1.5G illumination in air is more likely due to a chemical degradation in the materials rather than morphological changes, since otherwise a significant change of the PL spectrum is also expected for the samples undergoing light exposure in nitrogen.



Figure S5 Atomic force microscope images of a) as cast P3HT:O-IDTBR blend films, b) P3HT:O-IDTBR blend films after 8 hours of dark storage in air, and c) P3HT:O-IDTBR blend films after 8 hours of aging under AM1.5G conditions in air, with a RMS roughness of 20.35nm, 16.17nm and 22.58nm respectively. All blend films have been deposited on ITO/ZnO substrates films employing the same recipe as device fabrication.



Figure S6 UV-visible absorbance spectra of P3HT blend thin films photo-aged in dry air for up to 8 hours with a) PCBM, b) PC₇₁BM, c) BisPCBM, d) ICBA, e) ICTA, f) Eh-IDTBR, g) IDFBR and h) O-IDTBR.



Figure S7 UV-visible absorbance spectra of a) PCDTBT:PCBM, b) PBDB-T:PCBM, c) PCDTBT:O-IDTBR and d) PBDB-T:O-IDTBR blend thin films (~90 nm) prepared on quartz substrates and aged under AM1.5G illumination condition in dry air for up to 8 hours.



Figure S8 UV-visible absorbance spectra of a) PCDTBT:PCBM, b) PBDB-T:PCBM, c) PCDTBT:O-IDTBR and d) PBDB-T:O-IDTBR blend thin films (~90 nm) prepared on quartz substrates after storage in dark in dry air for up to 8 hours.



Figure S9 Transient absorption decays of thin films of (a) O-IDTBR recorded with 680 nm excitation and 1100 nm probe, (b) IDFBR recorded at 520 nm excitation and 1200 probe and (c) P3HT:IDFBR, 520 nm excitation and 1100 nm probe. IDFBR and O-IDTBR decays under O_2 were fitted with a single exponential function revealing monomolecular decay of triplet excitons quenched by O_2 . The P3HT:IDFBR transient absorption decay was successfully fitted with a power law function of the form a*tⁿ, indicating polaronic bimolecular decay and reactivity with oxygen on microsecond timescale.



Figure S10 Attempted power and exponential law fits of a) P3HT:O-IDTBR and b) P3HT:IDFBR transient absorption decays (from Figure 2 of the manuscript) demonstrating power law behaviour.



Figure S11 Evolution of the normalised absorbance peaks of P3HT neat and the P3HT contribution in blend films with different acceptors at 522 nm under AM1.5G illumination in dry air (RH<40%).



Figure S12 Evolution of the normalised absorbance peaks of different acceptors in blend films with P3HT under AM1.5G illumination in dry air (RH<40%). See Table S3 for the wavelength at which normalisation was performed for different blend systems).

Blend	Donor wavelength (nm)	Acceptor wavelength (nm)	
P3HT:PCBM	477	336	
P3HT:PC ₇₁ BM	470	241	
P3HT:BisPCBM	487	260	
P3HT:ICBA	468	250	
P3HT:ICTA	453	246	
P3HT:IDFBR	600	522	
P3HT:Eh-IDTBR	560	667	
P3HT:O-IDTBR	556	733	

Table S4 Wavelengths of donor and acceptor contributions of blend films for UV-Vis absorbance measurements in figures 4 and S7.



Figure S13 Cyclic voltammetry scans of HOMO level from which the LUMO level was calculated for acceptors: a) PCBM, b) PC₇₁BM, c) BisPCBM, d) ICBA, e) ICTA, f) O-IDTBR, g) Eh-IDTBR, h) IDFBR.



Figure S14 Fractional losses/changes of the absorbance peaks of the acceptors in blend films with P3HT after 8 hours of exposure under AM1.5G illumination in dry air (RH<40%) as a function of measured LUMO level of the acceptors. Fitted with exponential growth function $y = y0 + Ae^{((x-x0)/t)}$ (red line).



Figure S15 UV-visible absorbance spectra of neat P3HT thin film (~100 nm) aged under AM1.5G illumination condition in dry air for up to 30 minutes.



Figure S16 Negative ion mode MALDI-TOF measurement of a) fresh O-IDTBR (Mw=1326 m/z) and b) O-IDTBR aged in neat thin film (~ 100 nm) under AM1.5G illumination condition in dry air for 8 hours, undertaken by re-dissolving the films after photo-aging in air, revealing ~4% of photo-oxidised products (up to addition of 2 oxygen atoms) formed in conjunction with modest fragmentation upon 8 hours of light exposure in air.