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

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

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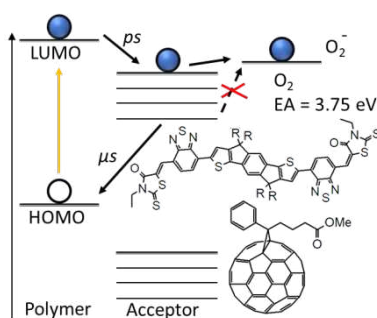
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With the emergence of non-fullerene electron acceptors resulting in further breakthroughs in the performance of organic solar cells, there is now an urgent need to understand their degradation mechanisms in order to improve their intrinsic stability through better material design. In this study, we present quantitative evidence for a common root cause of light-induced degradation of polymer:non-fullerene and polymer:fullerene organic solar cells in air, namely a fast photo-oxidation process of the photoactive materials mediated by the formation of superoxide radical ions, whose yield is found to be strongly controlled by the lowest unoccupied molecular orbital (LUMO) levels of the electron acceptors used. Our results elucidate the general relevance of this degradation mechanism to both polymer:fullerene and polymer:non-fullerene blends and highlight the necessity of designing electron acceptor materials with sufficient electron affinities to overcome this challenge, thereby paving the way toward achieving long term solar cell stability with minimal device encapsulation.



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3 The recent emergence of non-fullerene acceptors (NFAs) has reinvigorated the field of organic
4 solar cells (OSCs), with their device efficiencies rocketing from ~3% to over 17% over the past
5 3-4 years,¹⁻³ already exceeding the threshold for commercial viability. In addition to
6 potentially reduced material complexity and fabrication costs compared to fullerene
7 derivatives, this class of electron acceptor materials further possess excellent optical and
8 electrical properties owing to their highly tuneable molecular structures. The synthetic
9 flexibility of NFAs allows their optical bandgap to be tuned, allowing the light harvesting
10 properties to be optimised in chosen spectral regions, e.g. NIR or UV. The opportunity to tune
11 the molecular orbital energetics of NFAs also facilitates the engineering of devices with open
12 circuit voltages of over 1.1 eV and a remarkably low voltage loss.⁴⁻⁵

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17 With the majority of research effort still dedicated to taking advantage of the flexibility of
18 NFAs to optimise device efficiencies, the implications for the stability of fullerene-free OSC
19 are almost completely unclear. A small number of studies have demonstrated improved
20 lifetimes of fullerene-free OSCs under isolated environmental stress conditions (e.g. light-
21 soaking, thermal) compared to their fullerene-based counterparts,⁶⁻⁷ without further
22 evaluating their stability under mixed environmental stress factors relevant to standard
23 operating conditions, or elucidating their detailed degradation mechanisms. While the
24 exposure to molecular oxygen and illumination has been identified as a critical environmental
25 stress factor for fullerene-based OSCs,⁸⁻⁹ its impact upon fullerene-free OSC remains unclear
26 and has not been addressed to date. It has previously been established that two main
27 pathways for oxygen-induced degradation exist in fullerene-based OSCs: through singlet
28 oxygen (¹O₂) generation via energy transfer from triplet excited states and superoxide (O₂⁻)
29 generation via photoinduced transfer of electrons from the fullerene to molecular oxygen.¹⁰⁻
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12 We have demonstrated that for polymer:PCBM blends, degradation is dominated by the
pathway of triplet-induced singlet oxygen generation either through the polymer¹³ or the
fullerene¹⁴ component, while the pathway of superoxide formation is suppressed due to a
deep lying LUMO level of PCBM. In particular, we have further demonstrated that the
degradation of fullerenes, primarily through a light-induced oxidation process, can have a
drastic impact upon the stability of benchmark polymer:fullerene OSCs by significantly
altering the electron transport and recombination kinetics.⁸ However the relevance of these
degradation mechanisms for fullerene-free OSCs remains unknown, and strategies on
mitigation of these potential mechanisms have not been taken into account in the
development of NFAs, which offer a higher synthetic and energetic flexibility than fullerenes.
The development of robust design rules for the long term stability of fullerene-free OSCs will
enable their simultaneous advances in stability and performance.

Herein, we investigate the light-induced degradation of a range of polymer:fullerene and
polymer:non-fullerene OSC systems (see Figure S1 for chemical structures and fully chemical
names for all the materials investigated), and found that their stability under light and oxygen
is strongly correlated to the energy of the lowest unoccupied molecular orbital (LUMO) levels
of the electron acceptors used. We present direct evidence linking this correlation to a fast
(within ~10s of minutes of degradation) photo-oxidation process of the photoactive materials

(including both the donor and acceptor materials), mediated by the formation of superoxide radical ions with molecular oxygen in the environment through the electron acceptors. These results unravel the critical role of energetics of the electron acceptors in environmental stability, in addition to device efficiency, of both fullerene-based and fullerene-free OSCs. Our findings highlight the importance of taking stability into account in the material design of fullerene and non-fullerene acceptors, and provide a promising route in the development of high performance and environmentally stable OSCs.

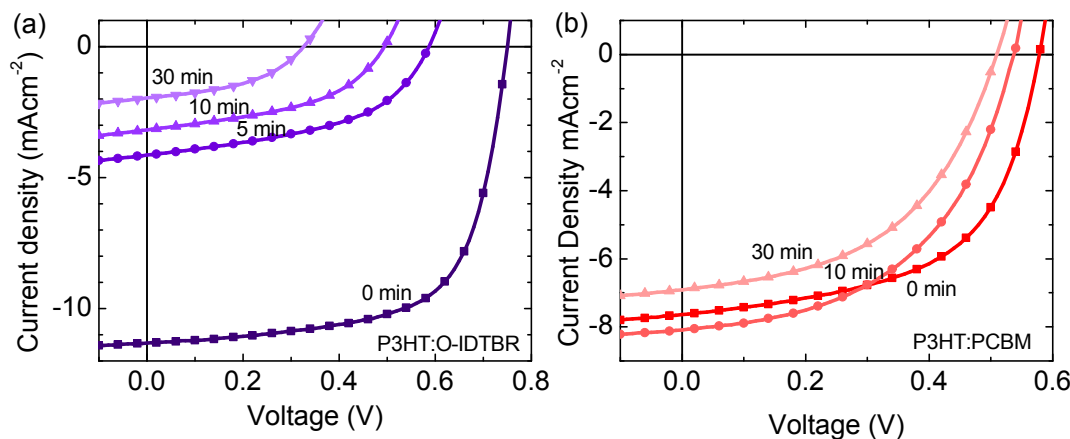


Figure 1 Current density-voltage (J-V) characteristics of OSCs with a structure of a) ITO/ZnO/P3HT:O-IDTBR/MoO₃/Ag and b) ITO/ZnO/P3HT:PCBM/MoO₃/Ag, undergoing different photo-aging times under simulated AM 1.5G illumination in dry air prior to electrode deposition.

The environmental stability of a benchmark fullerene-free OSC comprising P3HT:O-IDTBR was compared to P3HT:PCBM under exposure to light and air. P3HT:O-IDTBR represents one of the most promising fullerene-free OSC systems for commercialisation to date, combining potential advantages such as low cost, good upscalability and “burn-in” free photostability in an inert atmosphere, with large area, industry-compatible solar modules already demonstrated.¹⁵ For the device stability studies presented herein, exposure prior to back contact deposition was performed to allow the experiments to focus on the underlying photochemical degradation of the active layer, excluding any effects of oxygen diffusion. It has previously been shown that the degradation of complete devices capped with an oxygen blocking top contact takes much longer than uncapped devices, due to oxygen diffusion limitations.¹⁶ It is obvious that P3HT:O-IDTBR devices undergo rapid, drastic degradation, losing over 80% of their initial performance upon only 10 minutes photo-aging time, further increased to ~ 95% loss after 30 min of exposure (Figure 1a). In comparison, P3HT:PCBM devices undergo significantly less degradation, still retaining ~70% of their initial device performance upon 30 min of exposure (Figure 1b). The device characteristics of both OSC systems during degradation are summarised in Tables S1 and S2. Since the devices were degraded prior to electrode deposition, molecular oxygen was removed from the systems and the degradation observed is due to the photo-oxidation of the photoactive layers rather than oxygen acting as an electron traps. The J-V characteristics of P3HT:O-IDTBR devices under

dark storage in air or under exposure to AM1.5G conditions in nitrogen for 10 minutes were also measured as control experiments (Figure S2, Table S3), both revealing negligible changes in device efficiency, indicating that the rapid degradation of device efficiency in Figure 1a is primarily due to the combined exposure of light and oxygen, rather than light exposure or oxygen exposure alone.

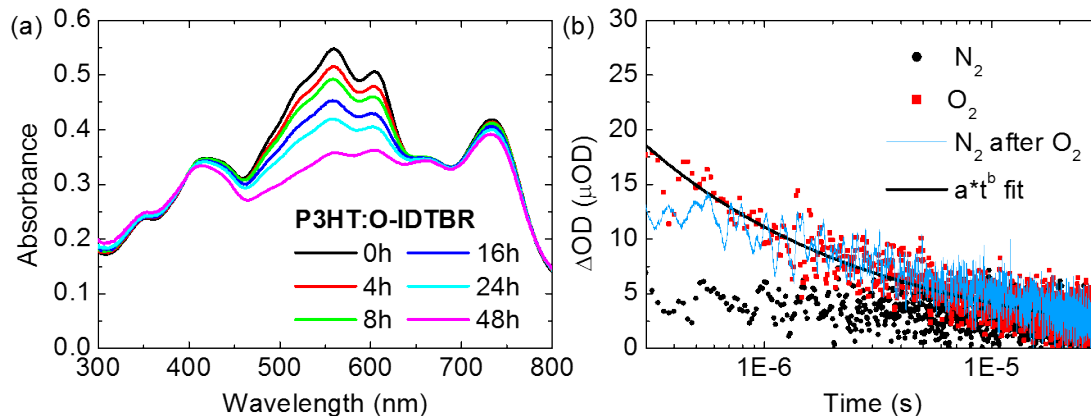
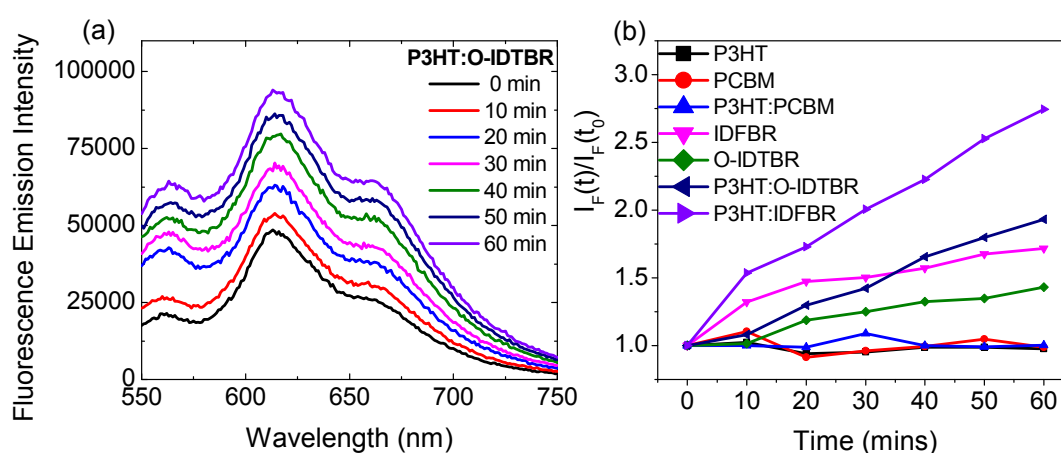


Figure 2 a) UV-visible absorbance spectra of P3HT:O-IDTBR blend thin films photo-aged in dry air for up to 48 hours. b) Transient absorption kinetics of P3HT:O-IDTBR blend film recorded under nitrogen (N_2), oxygen (O_2) and again N_2 atmosphere (excited at 500 nm and probed at 1060 nm). Black lines correspond to a fit to the data with a power law function, producing an exponent of -0.43 for N_2 decay, revealing the polaron's reactivity with O_2 . To investigate the origin of the rapid degradation of P3HT:O-IDTBR devices, UV-Visible, photoluminescence (PL), atomic force microscope (AFM), and transient absorption spectroscopy measurements of the blend thin films were performed. As shown in Figure 2a, P3HT:O-IDTBR films undergo rapid photobleaching under white illumination in dry air, with a loss of the absorbance peak at ~ 550 nm indicating the degradation of P3HT, whereas O-IDTBR only undergoes modest degradation. In comparison, minimal degradation of both P3HT and O-IDTBR is seen in the UV-visible absorbance spectra of P3HT:O-IDTBR blend thin films under light exposure in nitrogen or under dark storage in air (Figure S3). PL spectra and AFM images of the P3HT:O-IDTBR blend films (Figure S4 and S5b) reveal negligible morphological changes upon dark storage in air or photo-aging in air. It thus appears that the degradation of P3HT:O-IDTBR films and devices are primarily caused by the chemical degradation of P3HT due to the combined exposure of light and oxygen, with O-IDTBR showing less degradation than P3HT, although with some variations depending upon the experiment details. In comparison, P3HT:PCBM films exhibit significantly less photobleaching upon photo-aging for the same duration (Figure S6a), where the rapid degradation of P3HT compared to the acceptor was also absent. To further investigate the generality of this effect, we performed photobleaching studies for two other benchmark donor polymer systems, namely PCDTBT and PBDB-T (Figures S7 and S8), with the results in excellent agreement with the photobleaching kinetics of P3HT-based blend films (Figure S6). We further note that the photobleaching of the blend films occurs at a greater timescale than the devices, commensurate with previous studies.^{8,12-14} The different timescale can be understood by the degradation of completed solar cells being typically much more sensitive to materials degradation, the magnitude of which,

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3 however, may be too small to be detectable by optical measurements. Figure 2b shows the
4 polaron absorption decay of a P3HT:O-IDTBR blend film recorded under dry nitrogen and dry
5 oxygen environments. The signal assignment is based on successful fitting of the N₂ decay to
6 a power law function ($\Delta OD = At^{-n}$)¹⁷⁻¹⁸ which is characteristic of trap-assisted bimolecular
7 recombination of photogenerated polarons, which in chemical terms indicates
8 photogeneration of radical ions in the film. The observed quenching by O₂ therefore suggests
9 radical ion reactivity with ambient O₂. Such oxygen reactions are reported for
10 polymer:fullerene blends with acceptors with a LUMO energy higher than PCBM,¹² as is the
11 case for O-IDTBR, and are typically assigned to generation of superoxide, O₂⁻ via electron
12 transfer from the photogenerated fullerene radical ions to O₂. The data therefore suggests
13 that the P3HT:O-IDTBR blend is sensitive to molecular oxygen and likely forms O₂⁻ via electron
14 transfer from photogenerated O-IDTBR radical ions, further confirmed by the data in Figure 3
15 below. In comparison to P3HT:O-IDTBR, the transient absorption signal of the neat O-IDTBR
16 film (Supplementary Figure S9a) shows a single exponential decay with a time constant of
17 0.33 μ s under inert nitrogen environment, which is consistent with triplet exciton absorption,
18 further consistent with the degradation of O-IDTBR neat films upon photo-aging (Figure 2a).
19 The observed quenching of the triplet signal (on the hundred nanosecond timescale) can be
20 understood in terms of energy transfer from O-IDTBR's triplet to O₂ to generate singlet oxygen.
21 Supplementary Figure S9b-c present the results from the transient absorption study of IDFBR
22 and P3HT:IDFBR films, which similarly indicate mechanisms of singlet oxygen and superoxide
23 generation identical to those found for O-IDTBR and P3HT:O-IDTBR. The P3HT:IDFBR blend
24 film undergoes degradation during TAS measurements under an O₂ environment qualitatively
25 agreeing with its much higher instability compared to the P3HT:O-IDTBR blend. Figure S10
26 shows the result of power law and stretched exponential fits to P3HT:O-IDTBR and
27 P3HT:IDFBR transient absorption decays (from Figure 2, confirming their power law behaviour).



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Figure 3 (a) Fluorescence spectra of the HE probe in the presence of a P3HT: O-IDTBR blend film as a function of illumination time, and (b) Normalised fluorescence intensity increase of HE probe in the presence of neat and blend films at 610 nm (excited at 520 nm) as a function of illumination time under AM1.5G illumination condition in dry air (RH<40%). $I_F(t)$ is the

fluorescence maximum at time t , while $IF(t_0)$ is the background fluorescence intensity. $IF(t)/IF(t_0)$ corresponds to the yield of superoxide generation.

To investigate the formation of superoxide, fluorescent molecular probe studies were performed as previously.^{19,20} Hydroethidine was employed as the molecular probe due to its selective reactivity with superoxide ions to form ethidium, a fluorescent compound ($\lambda_{\text{excitation}} = 520 \text{ nm}$ and $\lambda_{\text{emission}} = 610 \text{ nm}$), insensitive to singlet oxygen, hydroxyl radicals, H_2O_2 or nitrogen radicals.²⁰⁻²² Moreover, at a given illumination time, it provides a measure of the amount of superoxide generated by the sample. In particular, this probe has been recently used to study superoxide generation in hybrid perovskites¹⁹ but here we use it to track O_2^- generation in semiconducting polymers and small molecules. Figure 3a shows typical fluorescence spectra of the molecular probe for P3HT: O-IDTBR as a function of illumination time, consistent with the spectra previously measured.²⁰⁻²² The increase in the fluorescence signal with longer photo-aging time provides direct evidence for an increasing yield of superoxide formation as a function of illumination time. We further extend our studies to various neat and blend films of P3HT and/or fullerene/non-fullerene acceptors, with a master plot of evolution of the superoxide formation shown in Figure 3b. It is obvious that the amount of superoxide formation is strongly dependent upon the types of acceptors used, with O-IDTBR and IDFBR-based neat and blend films showing the highest yield of superoxide formation and PCBM-based films showing the least. The blending of the acceptors with P3HT also has a strong impact, with for example, P3HT:IDFBR film producing the highest amount of superoxide, 1.6 times more than the neat IDFBR film (2.74 and 1.72 respectively). The P3HT:O-IDTBR film generates 1.4 times more superoxide than the neat O-IDTBR film (1.93 and 1.43 respectively). These results correlate well with the TAS data which shows that the blend films have a greater yield of longer-lived polarons which can react with oxygen to form the superoxide. In contrast, P3HT, PCBM and P3HT:PCBM films did not enhance the fluorescence of the molecules, implying no significant formation of superoxide, in agreement with previous studies.¹³

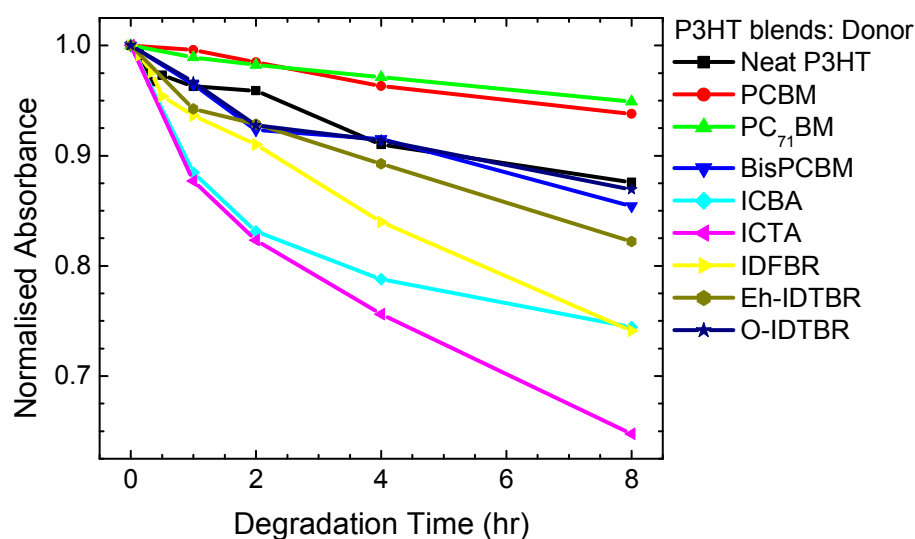


Figure 4 Evolution of the normalised P3HT absorbance peaks (see Table S4 for the wavelength at which normalisation was performed for different blend systems) in blend films with

different electron acceptors under AM1.5G illumination in dry air (RH<40%). Evolution of the P3HT absorbance normalised at the same wavelength of 522nm and of the electron acceptor absorption peaks, were also plotted as comparison in Figure S11 and S12 respectively.

To investigate the role of superoxide upon the degradation of the photoactive materials, photobleaching measurements (measured by a loss of absorbance upon degradation) were performed. Figure 4 shows the evolution of P3HT photobleaching (measured by a loss of the P3HT absorbance in the blend film) in blend with various types of fullerene and non-fullerene acceptors, revealing a strong dependence of the photobleaching of P3HT on the blending acceptors. It is obvious that P3HT shows minimal photobleaching in blend with PCBM and PC₇₁BM, while showing more pronounced photobleaching in blends with other fullerene acceptors such as Bis-PCBM, ICBA, ICTA and non-fullerene acceptors such as IDFBR, O-IDTBR and Eh-IDTBR. It thus appears that the superoxide formed upon photo-aging can cause degradation of P3HT, with the severity of degradation consistent with the measured quantity of superoxide in Figure 3. The superoxide formed in the blend film can also cause material degradation of the electron acceptors (Supplementary Figure S6) albeit with a greater variation than that of P3HT, likely due to the dependence of their photobleaching upon their molecular stability.

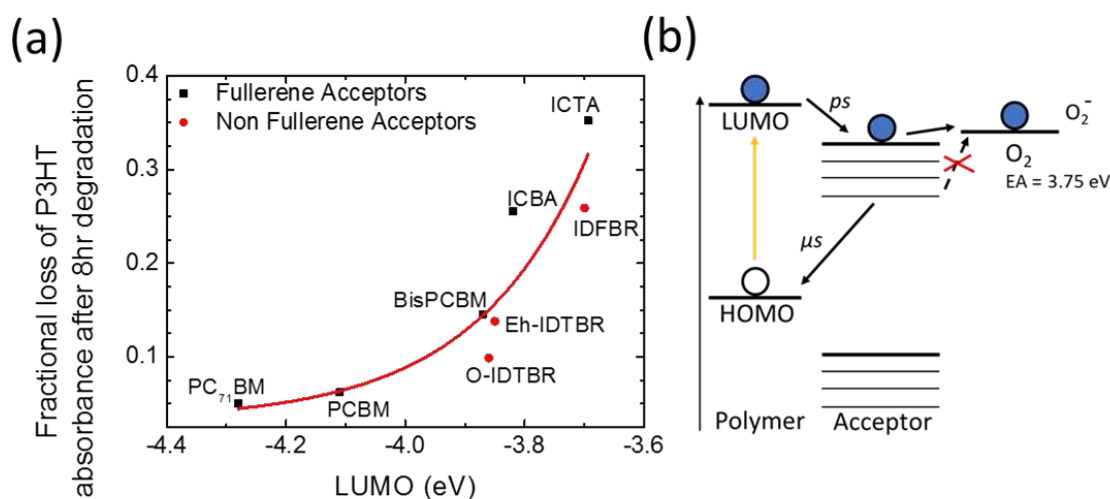


Figure 5 (a) Fractional losses of the P3HT absorbance peaks in blend films after 8 hours of exposure under AM1.5G illumination in dry air (RH<40%) as a function of measured LUMO level of the acceptors, fitted with exponential growth function $y = y_0 + Ae^{((x-x_0)/t)}$ (red line) and (b) the proposed degradation mechanism, namely the photodegradation of P3HT caused by the formation of superoxide (O₂⁻) via electron transfer from the LUMO levels of the acceptors to molecular oxygen (O₂) which has an electron affinity (EA) of 3.75 eV.

The fluorescent molecular probe and photobleaching measurements reveal a strong acceptor dependence of the stability of the photoactive materials in the blend films, whose degradation is found to be linked with superoxide formation. To quantify this strong dependence on the blending acceptors, we plot the amount of photobleaching of both P3HT and acceptors in the blend films upon 8 hours of exposure under AM1.5G illumination

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3 condition in dry air as a function of the LUMO levels of the neat acceptors (measured with
4 cyclic voltammetry, see Figure S13 for full data set). It is shown in Figure 5a that the
5 photobleaching of the P3HT in the blend films correlates very well with the LUMO of the
6 fullerenes and NFAs, with shallower LUMO levels of the acceptors resulting in more
7 photobleaching of P3HT in the blend films. The data can be fitted with an exponential growth
8 function due to the Boltzmann dependence of the electron transfer to the molecular oxygen
9 ground state being dependent on the LUMO energy of the acceptor. The correlation between
10 the photobleaching of the P3HT in the blend films and the LUMO levels of the acceptors also
11 match excellently with the fluorescence spectra (Figure 3), and is fully supported by the
12 transient absorption and device stability measurements, confirming that the degradation of
13 P3HT in the blend is primarily controlled by the LUMO level of the acceptors. The superoxide
14 formed also has an analogous impact upon the acceptors themselves, with a raised acceptor
15 LUMO level generally leading to more degradation (Supplementary Figure S14). Based on
16 these findings, we propose a common photodegradation mechanism of OSC blend films
17 mediated by the LUMO energy levels of electron acceptors (Figure 5b). A shallow LUMO level
18 of the acceptor facilitates the transfer of electrons to molecular oxygen to form superoxide,
19 which in turn reacts with both the electron donors and acceptors evidenced by strong
20 photobleaching in the blend films (e.g. P3HT:IDFBR). For electron acceptors with deeper
21 LUMO levels this process is energetically less favourable and is therefore suppressed (e.g.
22 P3HT:PCBM). This process appears to be general, and is independent of whether fullerene
23 acceptors or non-fullerene acceptors are used. In addition, electrons at the LUMO level of the
24 acceptor can also originate from direct photo-excitation of the acceptor, and is more likely to
25 occur in non-fullerene blend films, due to their typically stronger optical absorption than
26 fullerene acceptors. Furthermore, we note that the degradation of the acceptors shows
27 greater variations than that of the P3HT, suggesting that their degradation may be influenced
28 by additional factors. For example, we have reported elsewhere that the degradation of O-
29 IDTBR and IDFBR is also strongly dependent upon their molecular conformation, in addition
30 to their LUMO levels.

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33 Unravelling the degradation mechanisms under various environmental stress factors, in
34 particular under light and oxygen exposure, is fundamental to further advancing the material
35 design of OSCs to achieve long term environmental stability. Concerning photochemical
36 degradation, Hoke et al. proposed a light and oxygen induced degradation mechanism of
37 fullerene-based OSCs due to the photo-oxidation of polymers caused by fullerene-mediated
38 superoxide formation.¹² However, mitigation strategies of this degradation mechanism have
39 not been taken into account in the energetic design of NFAs, with the majority of high
40 performance NFAs (e.g. ITIC, IDTBR) developed to date possessing a shallower LUMO level
41 than PCBM and PC₇₁BM. Herein, we report an in-depth analysis of the degradation kinetics of
42 benchmark polymer:fullerene and polymer:non-fullerene blend systems, including
43 photobleaching and cyclic voltammetry measurements for a broad range of fullerene and
44 non-fullerene acceptors, as well as a range of advanced optical, chemical and device stability
45 studies for selected representative systems. We present direct, quantitative evidence to

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3 demonstrate that a raised LUMO level of the acceptors above the threshold for molecular
4 superoxide formation will lead to reduced photochemical stability of OSCs by facilitating a
5 fast photo-oxidation process (on the minute timescale) of not only the polymer donor, but
6 also the acceptor themselves. We further extend the generality of our conclusion to fullerene-
7 free OSCs, whose degradation mechanisms under light and oxygen exposure conditions, to
8 the best of our knowledge, have not been previously addressed.

9
10 A widely held hypothesis in the material and device design of OSCs is that individually stable
11 photoactive materials are a good indication of the environmental stability of complete OSCs.²³
12 For example, it is expected that P3HT:O-IDTBR blends should possess good environmental
13 stability, since both neat P3HT and O-IDTBR show fair material stability under exposure to
14 light and oxygen (evidenced by the modest photobleaching of neat P3HT as shown in Figure
15 S15, and Mass Spectrometry data of neat IDTBR in Supplementary Figure S16). Here we
16 demonstrate that good photochemical stability of individual photoactive materials is not
17 necessarily a good guideline for superior stability of OSCs under the same degradation
18 conditions, since the blending of individual materials could turn on additional critical
19 degradation pathways. For polymer:PCBM blends, the light and oxygen induced degradation
20 is primarily driven by singlet oxygen generation from polymer triplet states, with this pathway
21 being suppressed in P3HT:PCBM blends due to the short triplet lifetime of regio-regular P3HT
22 and the relatively slow degradation of P3HT:PCBM blends observed herein most likely
23 originating from PCBM triplet-induced singlet oxygen generation.^{8, 13-14} When the LUMO level
24 of the acceptor is raised, however, a different degradation pathway based on superoxide
25 generation turns on. This is of particular relevance to polymer:non-fullerene OSCs due to ease
26 of tunability of the energetics of non-fullerene acceptors. This degradation pathway is less
27 critical for conventional fullerene-based OSCs, whereby the formation of superoxide is
28 suppressed due to a deeper lying LUMO energy level of PCBM or PC₇₁BM.

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30 It should also be noted that currently the most widely used electron donors of fullerene-free
31 OSCs are still those originally optimised for fullerenes e.g. Poly(3-hexylthiophene) (P3HT),
32 PTB7-Th (PCE10), PffBT4T-2OD (PCE11) and PBDB-T (PCE12), with most high performance
33 non-fullerene acceptors developed to date optimised to match these (or energetically similar)
34 donor polymers.^{1, 6, 24-25} One such optimisation strategy has been designing non-fullerene
35 acceptors with a raised LUMO level in order to achieve a higher V_{oc} (hence power conversion
36 efficiency) by creating a higher donor HOMO/acceptor LUMO offset. We have demonstrated
37 that such strategy may lead to a significant decrease in the photochemical stability of the
38 resulting OSCs by significantly increasing the yield of superoxide formation. Our results
39 highlight the complexity in the material design to simultaneously achieve superior efficiency
40 and stability of OSCs. A redesign of the non-fullerene accepters with deeper LUMO energy
41 levels, as well as their matching donor polymers with deepened HOMO levels to compensate
42 the V_{oc} loss, might be a promising route toward the development of both efficient and
43 environmentally stable fullerene-free OSCs.

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45 In conclusion, we present a range of advanced optical, chemical and device stability
46 measurements to investigate the degradation mechanisms of benchmark fullerene-based and
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3 fullerene-free OSCs. We establish the critical correlation between the LUMO level of the
4 fullerene and non-fullerene electron acceptors and the resulting environmental stability of
5 OSCs and blend films strongly mediated by the yield of superoxide formation. Our results
6 highlight the need of redesigning electron acceptor materials with deepened LUMO energy
7 levels, as well as their donor polymers with deepened HOMO levels to overcome the
8 challenge of simultaneously improving device efficiency and stability, thereby paving the way
9 toward simultaneously achieving the high efficiency and long term environmental stability of
10 OSCs.
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16 **Supporting Information:**

17 Experimental details and additional experimental data.

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