

The Role of Electron Affinity in Determining Whether Fullerenes Catalyze or Inhibit Photooxidation of Polymers for Solar Cells

Eric T. Hoke, I. T. Sachs-Quintana, Matthew T. Lloyd, Isaac Kauvar, William R. Mateker, Alexandre M. Nardes, Craig H. Peters, Nikos Kopidakis, and Michael D. McGehee*

Understanding the stability and degradation mechanisms of organic solar materials is critically important to achieving long device lifetimes. Here, an investigation of the photodegradation of polymer:fullerene blend films exposed to ambient conditions for a variety of polymer and fullerene derivative combinations is presented. Despite the wide range in polymer stabilities to photodegradation, the rate of irreversible polymer photobleaching in blend films is found to consistently and dramatically increase with decreasing electron affinity of the fullerene derivative. Furthermore, blends containing fullerenes with the smallest electron affinities photobleached at a faster rate than films of the pure polymer. These observations can be explained by a mechanism where both the polymer and fullerene donate photogenerated electrons to diatomic oxygen to form the superoxide radical anion which degrades the polymer.

terephthalate) (PET) and poly(ethylene naphthalate) (PEN) have oxygen and water vapor transmission rates that are several orders of magnitude larger than the recommended transmission requirements for organic photovoltaics of $10^{-3} \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$ and $10^{-4} \text{ g m}^{-2} \text{ day}^{-1}$, respectively.^[1] Multilayered composite barrier materials consisting of alternating metal oxide and polymer layers have achieved these required permeabilities,^[6] and flexible OPV devices based on these laminates have demonstrated comparable stabilities to glass encapsulated devices.^[7] However, bringing the cost of these complex flexible barrier materials below $\$10 \text{ m}^{-2}$ poses a significant challenge. Understanding how to improve the intrinsic stability of the active layer material of OPV devices may

reduce the permeability requirements and cost of flexible barrier layers as well as increase the lifetime of devices.

It is well known that most semiconducting polymers photobleach in the presence of oxygen. Multiple studies in the past five years have demonstrated that photooxidation of many semiconducting polymer films used for OPV proceeds by a radical mechanism.^[8,9] The superoxide radical ion O_2^- , formed by electron transfer from the photoexcited polymer to diatomic oxygen, has been proposed as a primary initiator to polymer photodegradation.^[10]

Photogenerated O_2^- from PPVs in the presence of oxygen has been observed by electron spin resonance^[10] and the rate of photobleaching of PPV's has been shown to increase when blended with dicyanoanthracene, which is known to produce the radical superoxide anion in the presence of light and oxygen.^[9,10] Photodegradation of MDMO-PPV^[11] and P3HT^[12] has been proposed to occur by free radical abstraction of hydrogen at the alpha position of the side-chains based on Fourier transform infrared (FTIR) spectroscopy studies and the well known reactivity of these positions to deprotonation.^[13] In the case of MDMO-PPV, concurrent deprotonation at the alpha position enables oxygen to react with the vinyl group on the polymer backbone, ultimately resulting in chain scission.^[8,9] Although it has been shown that singlet oxygen can cause semiconducting polymers to photobleach in solution,^[14,15] recent studies have concluded that this is not the dominant mechanism in solid films for the most studied photovoltaic polymers. MDMO-PPV

1. Introduction

Organic photovoltaics (OPVs) offer the potential of providing energy at a significantly lower cost than conventional inorganic technologies due to the advantages of high throughput solution-based roll-to-roll processing, low materials costs, and facile installation of light weight, flexible modules.^[1–3] Recently there have been multiple reports of power conversion efficiencies of over 8% for polymer-fullerene bulk heterojunction solar cells^[4] and a lifetime approaching 7 years was demonstrated for glass encapsulated devices based on polymer-fullerene blends of PCDTBT and PC₇₁BM.^[5] However, in order to take full advantage of the cost reductions of organic solar cells from roll-to-roll printing, devices need to be made on inexpensive flexible substrates that provide a sufficient barrier layer to oxygen and water. Commercial plastic substrates such as poly(ethylene

E. T. Hoke, I. T. Sachs-Quintana, I. Kauvar,
W. R. Mateker, Dr. C. H. Peters, Prof. M. D. McGehee
Department of Material Science and Engineering
Stanford University
476 Lomita Mall, Stanford, CA 94305, USA
E-mail: mmcgehee@stanford.edu

Dr. M. T. Lloyd, Dr. A. M. Nardes, N. Kopidakis
National Renewable Energy Laboratory
1617 Cole Blvd, Golden, CO 80401, USA



DOI: 10.1002/aenm.201200169

and P3HT were exposed to singlet oxygen, either generated by sensitization^[9] or in large doses chemically,^[16] and showed no increase in photobleaching rate compared to control devices.

The most commonly used acceptor in polymer solar cells, PCBM has been shown to greatly slow the rate of photooxidation of MDMO-PPV^[8,17] and P3HT^[18] in the presence of oxygen. PCBM has also been shown to virtually halt degradation of P3HT in the dark in the presence of oxygen,^[18] and slow photobleaching of MDMO-PPV in the absence of oxygen by a factor of ten.^[8] These observations have led to suggestions that PCBM stabilizes polymers from photooxidation as a radical scavenger,^[8,18] based on the well known ability of fullerenes to terminate free radical reactions.^[19] Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy^[18] and FTIR^[8] have shown that PCBM in blend films is also oxidized in the presence of oxygen and light which suggests that fullerenes may react with radical oxidizing species before they can attack the polymer.

Multi-adduct fullerene derivatives are a relatively new class of electron acceptor material that are typically less electronegative than the archetypal PCBM and consequently can raise the open circuit voltage of polymer-fullerene solar cells. In particular indene-C₆₀ bisadduct (ICBA)^[20] has been shown to improve the efficiency of P3HT based devices from 4% to 6.5% by raising the open circuit voltage.^[21] However, little is known to date about the stability of polymer:multiadduct-fullerene blends. In this report, we investigate the photobleaching dynamics for a variety of polymer:fullerene blend films. We find that the rate of photobleaching of the polymer absorption increases with decreasing electron affinity (EA) of the fullerene. In the case of blends containing the multiadduct indene fullerenes ICBA and indene-C₆₀ trisadduct (ICTA), the photodegradation rate

was found to be comparable or faster than that for the pure polymer. We perform photoluminescence, quasi-steady state photoinduced absorption (PIA) and FTIR spectroscopy measurements and show that these observations are consistent with a mechanism where both polymer and fullerene can donate photogenerated electrons to oxygen, creating the radical superoxide anion that initiates degradation of the polymer.

2. UV-vis Degradation Experiments

Films of a variety of pure polymers and 1:1 polymer:fullerene blends by weight, whose structures are shown in **Figure 1**, were aged under a LG sulfur plasma lamp exposed to the ambient atmosphere and their absorption spectra were periodically measured. The lamp provided an illumination intensity of 100 mW cm⁻² and a spectrum that contains little UV light but has a close spectral match to the AM 1.5G spectrum over the visible wavelengths (see Supporting Information (SI), Figure S5). The films had an initial peak optical density of around 0.3 to ensure the illumination intensity did not vary appreciably throughout the thickness of the film. Films of different polymers were found to photobleach at substantially different rates varying from minutes to days. **Figure 2a** shows the time evolution of P3HT:ICBA film absorption. After appreciable photobleaching of the polymer, the blend film absorption resembles the absorption spectra of pure fullerene films, which is more stable to photobleaching as has been shown in previous studies.^[18,22] The polymer photobleaching is attributed to a loss in conjugation along the polymer backbone, while oxidation of the fullerene cage is not expected to reduce absorption as appreciably. A loss in vibronic structure and a slight blueshift of about

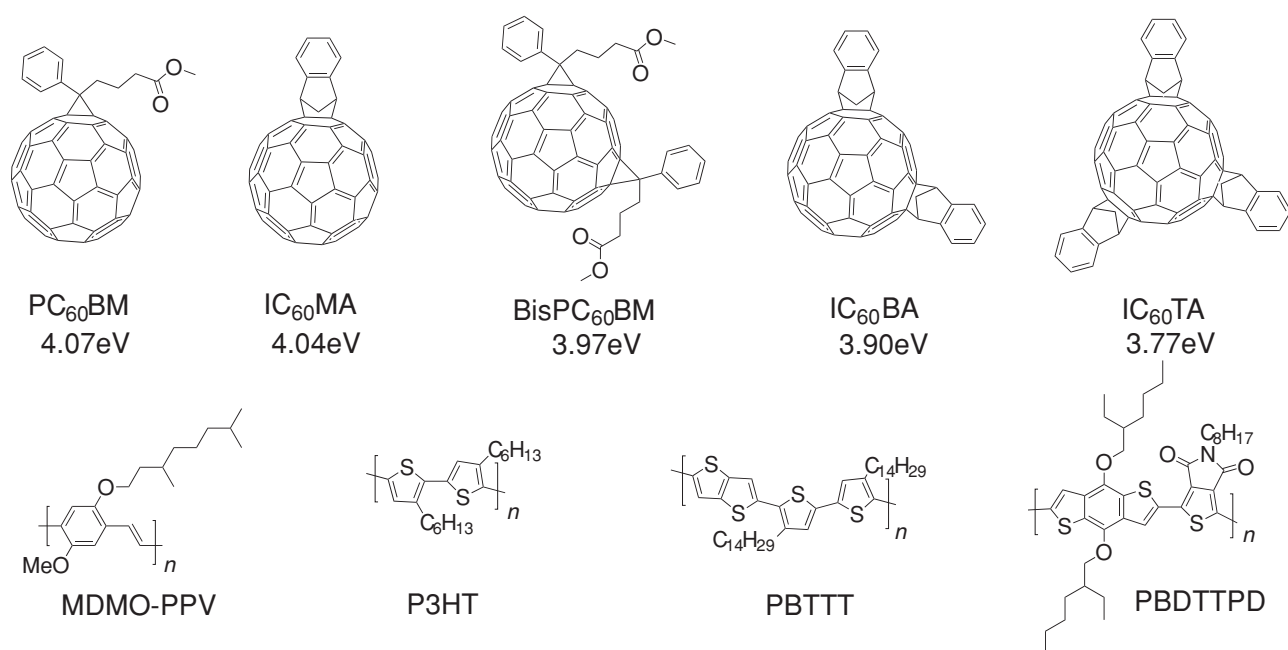


Figure 1. Chemical structures for the fullerenes and photovoltaic polymers considered in this study. The electron affinities of the fullerenes measured by cyclic voltametry are listed below the structures.

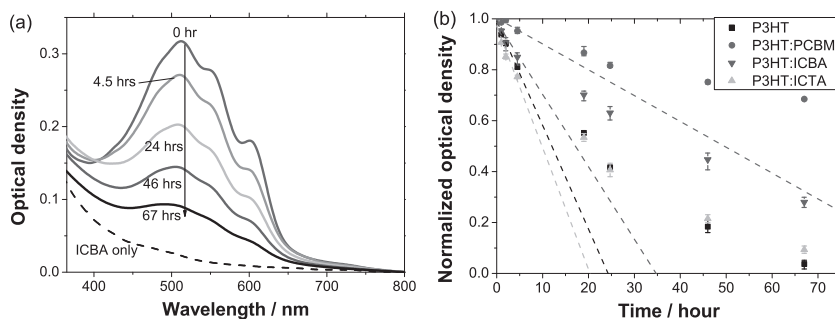


Figure 2. a) Absorption spectra of a P3HT:ICBA blend aged in ambient under 100 mW cm^{-2} illumination and of a pure unaged ICBA film. b) Polymer absorption at 520 nm for P3HT, P3HT:PCBM, P3HT:ICBA and P3HT:ICTA under illumination normalized by the initial maximum optical density before ageing. The error bars indicate the maximum and minimum values measured for the different equivalent samples. The dashed lines indicate the fitted rates from the first five hours of ageing.

10 nm (50 meV) is observed in the peak absorption by the P3HT component as the films are aged, which we attribute to a reduction in delocalization length along the polymer backbone. FTIR absorption spectra of the aged films indicate a dramatic appearance of carbonyl and hydroxyl groups around 1700 cm^{-1} and $3500\text{--}3000 \text{ cm}^{-1}$, respectively, indicating the polymer is oxidized as it photobleaches (see SI, Figure S1) which is consistent with other studies.^[12] In contrast, in the dark, the P3HT:PCBM blends showed a reduction in absorption of only 3% after 1500 h of ageing in air and all of the other P3HT containing films similarly retained more than 80% of their peak absorption. (SI, Figure S2).

The normalized optical density loss per hour was calculated for each blend by fitting the initial slope of the decay in the polymer absorption maxima, normalized by the initial peak absorption before ageing. The time period corresponding to the first 5–20% loss in optical density was used for the fit so that the absorption is mostly from the polymer and that the rate photons are absorbed did not substantially change over the time interval due to photobleaching. We found that for most of our samples the rate of photobleaching slows as the films are bleached and absorb less light (Figure 2b), as may be expected from a photo-initiated degradation mechanism, although other groups have reported photobleaching rates which remain constant even after the films are bleached by more than 50%.^[23,24] Based on the relative absorption coefficients of P3HT and PCBM^[25] we estimate that 92% of light absorption at 520 nm is absorbed by P3HT in the blend films. We chose to focus our study on fullerenes based on C_{60} to minimize absorption by the fullerene, though no significant difference in degradation rate was observed when PC_{60}BM was replaced by its C_{70} analog (not shown). As reported previously,^[18] the P3HT:PCBM photobleached at a slower rate ($1\% \text{ h}^{-1}$) than P3HT ($4.1\% \text{ h}^{-1}$). Surprisingly, we find that ICTA was found to accelerate the photobleaching rate of P3HT ($4.8\% \text{ h}^{-1}$). The accelerated photobleaching of P3HT:ICTA relative to P3HT was confirmed with a second batch of ICTA.

To determine why some fullerenes act as antioxidants towards polymer photobleaching while other fullerenes catalyze photooxidation, the rate of photobleaching was measured for a variety of blends of polymer and fullerenes. The photobleaching rates vary by several orders of magnitude between blends containing different polymers which is attributed to the wide range

in stability of the polymers.^[24] However, for each series of blends made with the same polymer, the polymer photobleaching rate strongly correlates with the electron affinity of the fullerene determined by cyclic voltammetry measurements (Figure 3). For all polymers considered, the polymer photobleaches slowest when blended with the largest electron affinity fullerene (PC_{60}BM) and degrades faster with decreasing electron affinity. During the preparation of this manuscript, we learned that a similar trend has been recently observed by another research group.^[26] For all of the polymers, ICTA and in some cases ICBA enhanced the polymer photobleaching rate while the other more electronegative fullerenes stabilized the polymer to photooxidation.

3. Discussion

3.1. No Direct Role for Singlet Excitons in Photodegradation

It has been suggested that PCBM stabilizes P3HT to photodegradation by quenching excitons on the polymer on a sub-picosecond time scale.^[17,18] We considered the possibility that differences in exciton quenching could account for the variation in degradation rates for the different fullerenes. The presence of multiple adducts reduces the electron affinity of fullerene, but these adducts can also affect the efficiency of exciton quenching by changing the morphology of the blend, for example by determining whether the fullerenes intercalate between the polymer side chains.^[27,28] While most single-adduct fullerenes can mix at a molecular level with many polymers, resulting in

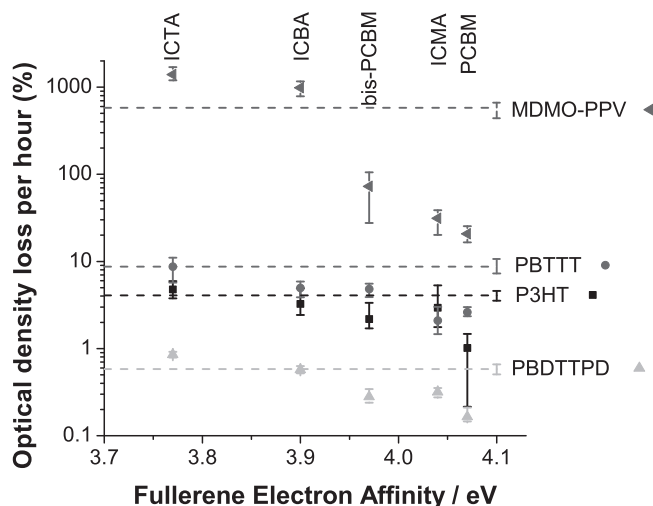


Figure 3. Photobleaching rate of blend films as a function of the fullerene electron affinity. The dashed lines indicate the photobleaching rate of the pure polymer films. The error bars indicate the maximum/minimum values measured for the different equivalent samples \pm a standard error in the fitted rate.

~99.9% singlet exciton quenching as observed by photoluminescence quenching studies, steric interactions prevent intercalation of multiadduct fullerenes such as bis-PCBM and ICTA resulting in lower exciton quenching efficiencies.^[28] Energetic considerations can also impact the exciton quenching efficiency as excitons will instead undergo energy transfer to the lower bandgap material if the driving force for charge transfer is too small. This results in unquenched photoluminescence from the fullerene when the polymer bandgap is larger than the fullerene (~1.7 eV) or from the polymer for blends with low-bandgap polymers.^[29] For example, polymer excitons were efficiently quenched due to charge transfer in blends of a low-bandgap polymer Si-PCPDTBT with PCBM but hardly quenched at all when blended with ICTA.^[29]

Steady-state photoluminescence measurements were performed to determine whether the variation in photobleaching rate by different fullerenes could be explained by differences in polymer singlet exciton quenching efficiency in the blend films. No correlation was observed between the electron affinity of the fullerene and the photoluminescence quenching efficiency (Table 1). Consequently, differences in exciton quenching cannot account for the dependence of polymer photobleaching rates on the fullerene electron affinity. The quenching efficiency of the bis-PCBM and ICTA containing blends are slightly lower compared to the other fullerenes for several of the polymers, because they cannot intercalate.^[28,30] However, we find that in all blends the polymer photoluminescence is quenched by 95% or more, with no observed fluorescence from the fullerene. The steady state population of singlet excitons on the polymer is thus at least 20 times higher in the pure polymer films than the ICTA containing blends. Since the ICTA blends degrade faster than the pure polymer films, these results suggest that polymer singlet excitons do not play the primary role in the polymer photobleaching mechanism.

3.2. The Role of Photogenerated Electrons in Photodegradation

The dependence of the polymer photobleaching rate on the electron affinity of the fullerene and not on the steady state

Table 1. Photoluminescence quenching efficiencies (%) of various polymer:fullerene blends.

Fullerene	Electron Affinity [eV]	MDMO-PPV	P3HT	PBTTT	PBDTTPD
PCBM	4.07	>99.9	98.8	99.9	>99.9
ICMA	4.04	99.8	98.4	99.8	>99.9
Bis-PCBM	3.97	>99.9	97.0	97.0	99.5
ICBA	3.90	>99.9	98.1	99.7	99.1
ICTA	3.77	99.8	94.7	96.5	97.0

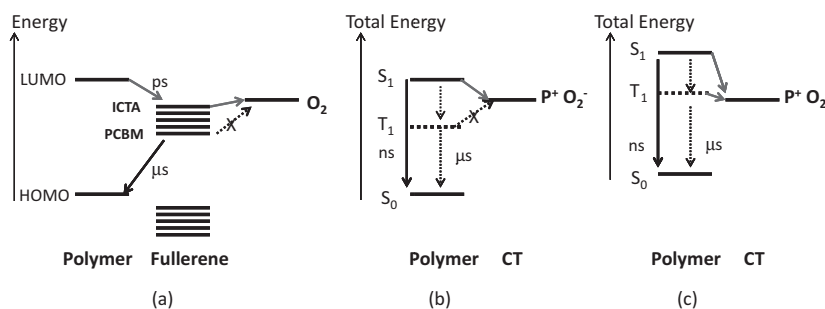


Figure 4. (a) Proposed mechanism for O_2^- generation from polymer:fullerene blends in the presence of oxygen represented on a HOMO/LUMO (highest occupied molecular orbital/lowest unoccupied molecular orbital) energy diagram. Microsecond charge recombination competes with electron transfer to O_2 (EA = 3.75 eV). The discrete acceptor energy levels represent increasingly electronegative fullerene derivatives investigated in this study, from ICTA (EA = 3.77 eV) to PCBM (EA = 4.07 eV). (b,c) Proposed mechanism for O_2^- generation from a pure polymer film represented on a Jablonski state diagram. Here nanosecond recombination of the singlet exciton competes with electron transfer from the polymer to oxygen to form a polymer-oxygen charge transfer (CT) state complex. For polymers with significant intersystem crossing yields and small electron affinities (c), triplet excitons on the polymer may also undergo charge transfer to oxygen and form O_2^- in substantial yield.

population of singlet polymer excitons suggests that photogenerated electrons are involved in the degradation mechanism. These observations can be explained by a mechanism where photogenerated electrons on the polymer or fullerene can transfer to diatomic oxygen, O_2 , forming the superoxide radical anion, O_2^- (Figure 4), which can then degrade the polymer. We measure a reduction potential for dissolved oxygen in chlorobenzene to be 3.75 eV below the vacuum energy after bubbling ambient air through the solution. This value is within the thermal energy of the ICTA electron affinity at 3.77 eV. We note that the reduction potential of diatomic oxygen in a film will depend upon the polarity of the environment. Hydrated forms of oxygen are easier to reduce than isolated O_2 ^[31] so additional oxidizing radicals may be generated in higher yield in the presence of water. This may explain why water has been shown to enhance the rate of photooxidation when O_2 is present, but has a small effect when no oxygen is present.^[23] The smaller the electron affinity of the fullerene, the more likely photogenerated electrons on the fullerene will transfer to oxygen to form a radical which initiates polymer degradation (Figure 4a).

We suggest that degradation is faster in pure polymer films than most of the polymer:fullerene blends because there is a sufficiently large energetic driving force for polymers to donate photogenerated charges to oxygen (Figure 4b). In contrast, electron transfer from most of the fullerenes to oxygen will not be energetically favorable and will not occur often. Electron transfer will more likely occur from O_2^- to these fullerenes, and thus the fullerene may be able to act as a radical scavenger. In the case of the more electropositive fullerenes, such as ICTA, there is a significant chance that photogenerated electrons will transfer from the fullerene to oxygen. In polymer:fullerene blends, photogenerated electrons experience lifetimes on the order of microseconds before they bimolecularly recombine with holes on the polymer. Hence, long-lived electrons in blends are more likely to encounter an oxygen molecule to create free radicals than in pure polymer films where photogenerated electron-hole

pairs relax to form excitons and typically recombine in a nanosecond. This could explain why the ICTA blends photobleach faster than the corresponding pure polymer films.

3.3. The Role of Polymer Triplet Excitons in Photodegradation

It has been proposed that triplet excitons can also initiate photooxidation of conjugated polymer films by undergoing electron transfer to form O_2^- .^[10] Although this may be a significant pathway for superoxide anion generation in some pure polymer films, our experimental data suggests that this is not an important pathway in efficient polymer fullerene blends for solar cell applications where triplet excitons are efficiently quenched. It has been demonstrated that in some bulk heterojunctions, and frequently in polymer-polymer blends,^[32,33] triplet excitons are formed in larger numbers when the triplet exciton on one of the materials is lower in energy than the charge transfer exciton between the two materials.^[34] We would therefore expect larger triplet populations in blends containing the least electronegative fullerene, ICTA, where the charge transfer energy is the largest and may be higher in energy than the triplet exciton on the polymer. Steady state photoinduced absorption spectra were measured on films of the pure polymer and blend films to determine relative steady state polymer triplet populations. The spectra for the P3HT containing films are shown in Figure 5. The P3HT $T_1 \rightarrow T_N$ triplet absorption is centered around 1.05 eV, while the P3HT hole polaron absorbs below 0.75 eV and above 1.1 eV.^[34] A shoulder is observed in the P3HT:ICTA blends around 1.05 eV which suggests the presence of some triplets in these blends. However the steady state population of triplets is a factor of four lower in the P3HT:ICTA blend film than in P3HT even though the blend film photobleaches faster. Triplet excitons also cannot explain the vastly different photobleaching rates of P3HT:PCBM and P3HT:ICBA, both of which have insignificant triplet populations, as expected from their high efficiency^[21] in solar cell devices.

We note that superoxide formation from triplet excitons may be the dominant photodegradation mechanism in pure polymer films, particularly those with large intersystem crossing rates and small electron affinities. To test this hypothesis, we examined the photobleaching dynamics of films containing the large bandgap (2.92 eV) polymer PFB which has

a significant triplet exciton yield of 3.4%^[32] in thin films. As shown in Figure 5b, the pure films of PFB photobleached more than ten times faster than all of the PFB:fullerene blends even though the number of photons absorbed by the blend films under the sulfur plasma lamp is about 30 times larger than in the pure PFB films, which hardly absorb any visible light (see SI Figure S5). PFB triplets are fully quenched in blends with various fullerenes resulting in charges or triplets on the fullerene.^[35] We propose that the significantly faster degradation in the PFB-only films may be due to the ability of long-lived triplet excitons in the polymer to generate O_2^- (Figure 4c). The electron affinity of PFB is extremely small (2.2 eV).^[36,37] Assuming that triplet excitons are 0.7 eV more stable than singlet excitons^[38] for PFB, there should still be a large driving force of ~ 0.85 eV for electron transfer from a polymer triplet exciton to oxygen (EA = 3.75 eV). In contrast, it may not be energetically favorable for triplet excitons to undergo electron transfer to oxygen in polymers with substantially larger electron affinities (Figure 4b). As with the other polymer blends considered in this study, the photobleaching rate of the PFB:fullerene blends increased with decreasing fullerene electron affinity, suggesting that photogenerated electrons on the fullerene likely also play a role in the photodegradation of these blends.

3.4. Future Outlook

The lower stability to photooxidation of blend films containing fullerenes with smaller electron affinities suggests that multi-adduct fullerenes may be less suitable for solar cell applications than conventional PCBM. Since these fullerenes were created to raise the open circuit voltage of devices, the development of more electronegative polymers may be a better strategy to raise the voltage of devices without sacrificing stability of the active layer. An additional strategy to reduce photooxidation of conjugated polymers is to design materials which are less reactive with anionic radicals such as O_2^- . As discussed previously, the α -hydrogen on the alkyl and alkyloxy side chains of many polymers is susceptible to extraction by radicals and can result in side chain oxidation, scission and the generation of additional radicals.^[11] Protecting these sites, perhaps by fluorination^[39] may prevent the propagation of these radical reactions and slow

photodegradation. One promising strategy is to remove the radical propagating side chains altogether by using polymers with thermocleavable side chains.^[40,41] Polymers which had their side chains removed by thermocleaving were shown to photobleach at a rate 2-20 times slower than the corresponding polymers with sidechains left intact.^[24]

It is currently unclear if the fullerene electron affinity has a significant impact on the degradation dynamics of well encapsulated solar cell devices or if the photooxidation of the active material is a dominant degradation mechanism in these devices. For example, glass encapsulated PCDTBT based devices were shown to experience an initial

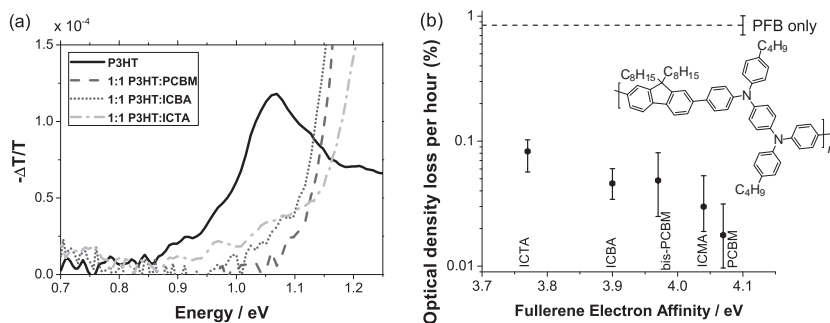


Figure 5. a) Quasi-steady-state photo-induced absorption (PIA) of P3HT containing films at 80 K. The samples were excited at 488 nm with a pump intensity of 80 mW cm⁻². b) Normalized photodegradation rates for polymer:fullerene blends containing the large bandgap polymer PFB (structure in insert). The dotted line represents the photodegradation rate for pure PFB films.

rapid degradation in efficiency over the first hundred hours of testing under illumination before stabilizing.^[5] These burn-in dynamics were demonstrated to occur only under illumination, and did not occur from applying a forward current to the device.^[5] If O_2^- generation from electrons on the fullerene were a significant degradation mechanism during burn-in, we would expect injected electrons to degrade the device just as easily as photogenerated electrons. It is thus unlikely that the processes discussed here describe burn-in in these devices. P3HT:PCBM devices with air stable electrodes were shown to degrade in efficiency when exposed to the presence of oxygen and light.^[42] Much of the loss in photocurrent could be recovered by annealing the devices, which was attributed to reversible photodoping of the polymer by O_2^- . Developing materials with larger electron affinities should make them both less receptive to photodoping and minimize permanent degradation caused by O_2^- .

4. Conclusion

We have demonstrated that the photobleaching rate of polymers in polymer:fullerene blends in the presence of oxygen depends critically upon the electron affinity of the fullerene. Polymers blended with fullerenes with smaller electron affinities degraded substantially faster than those with larger electron affinities. The most electropositive fullerenes (ICTA and in some cases ICBA) accelerated the rate of photobleaching for all of the photovoltaic polymers considered. These results are consistent with a mechanism where O_2^- or hydrated analogs can be generated by electron transfer from the polymer or the fullerene to oxygen. Designing polymers and fullerenes with larger electron affinities, and developing polymers which are more robust to attack from the superoxide radical anion may result in more stable devices which have less stringent requirements on the permeability of encapsulation materials.

5. Experimental Section

Materials: PBTTC- C_{14} , and PBDTPD were purchased from Solarmer Materials. Regioregular P3HT was purchased from Rieke Metals, MDMO-PPV was purchased from Sigma Aldrich and PFB was purchased from American Dye Source. PC₆₀BM, and bis-PC₆₀BM and were purchased from Nano-C. IC₆₀MA IC₆₀BA, IC₆₀TA were generously provided by Plextronics. All materials were studied as received without additional purification.

Sample preparation and ageing: Polymer and polymer:fullerene blend films were spin-cast onto glass substrates cleaned by sequential ultrasonication baths in detergent, water, acetone and isopropanol. Films were cast from dichlorobenzene (P3HT and PBTTC) and slow dried overnight or from chlorobenzene (all other materials) resulting in a peak optical density of approximately 0.3 so that the light intensity throughout the thickness of the film is relatively uniform. The samples were aged under a sulfur-plasma lamp (LG 6000 K) with an illumination intensity of 100 mW cm⁻² in air at 40 °C exposed to ambient humidity. At least three sample copies of each film were aged to provide statistics on the photobleaching process. All samples made with the same polymer were aged under the same lamp at the same time and were rotated after every measurement or at least every 12 h to control for small spatial variations in the collimated lamp output. UV-Vis spectra were measured periodically using an Agilent Cary Eclipse 6000i spectrophotometer.

Fourier-Transform Infrared (FTIR) spectroscopy was performed on a Bruker Vertex 70 spectrometer. FTIR samples were spin-cast onto silicon

substrates polished on both sides of the wafer. The silicon substrates were cleaned using the aforementioned procedure. The FTIR spectrums are an average of 200 scans.

Cyclic voltammetry was performed on dilute (~1 mg mL⁻¹) solutions of the fullerene derivatives in anhydrous chlorobenzene in a nitrogen glovebox environment using a CHI411 instrument from CH Instruments, Inc with tetra-n-butylammonium hexafluorophosphate (0.05 M, n-Bu₄NPF₆, from Strem Chemicals, Inc., recrystallized from ethanol) as the supporting electrolyte. The experiments were carried out using platinum working and counter electrodes and a Ag/AgCl wire as a pseudoreference electrode. Scans were performed at ambient temperature at a scan rate of 100 mV s⁻¹, though similar voltogram traces were observed at slower scan rates. The Fc/Fc⁺ redox couple was used as a reference oxidation potential for the electrochemical measurements. The electron affinity of the fullerenes was estimated by comparing the onset of the first reduction wave of the fullerenes to the onset of the oxidation of ferrocene and assuming a reduction potential of 5.1 V vs. vacuum for ferrocene.^[37] The voltograms for the fullerenes and air are shown in are shown in Figure S3 and S4 of the SI, respectively.

Photoluminescence spectra were measured as previously described.^[43] Quasi-steady state photoinduced absorption measurements were performed using an argon ion laser as the pump and the monochromated (Newport Cornerstone 260 with sorting filters) output of a mercury arc lamp (100 W, Newport 6281) as the probe beam. The pump beam was mechanically chopped at 575 Hz and the transmission of the probe beam was passed through a second monochromator and monitored using a silicon (Costronics 2005) or InGaAs (Thorlabs PDA 10D) photodetector. The change in transmission (ΔT) was measured using a lock-in amplifier (Stanford Research Systems SR830) while the transmission intensity (T) was simultaneously measured using a Keithley 2400. The measurement was repeated with the probe beam blocked to account for photoluminescence. PIA spectra were normalized by the fraction of the pump beam absorbed by the sample.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

E.T.H., I.T.S.Q., and M.T.L. contributed equally to this work. This publication was supported by the Center for Advanced Molecular Photovoltaics (Award No KUS-C1-015-21), made by King Abdullah University of Science and Technology (KAUST). M.T.L., A.M.N and N.K. acknowledge support from the US Department of Energy under Contract No. DE-AC36-08-GO28308 with the National Renewable Energy Laboratory through the DOE SETP program. We thank Plextronics for providing some of the fullerenes (ICMA, ICBA, and ICTA) and LG providing the sulfur plasma lamps. We thank H.-J. Egelhaaf for helpful discussions. Additional support was provided for E.T.H. by the Fannie and John Hertz Foundation, for I.T.S.Q. by the National Science Foundation Graduate Research Fellowship and I. K. was supported by the DOE SULI fellowship program.

Received: March 9, 2012

Published online: May 21, 2012

- [1] M. Jørgensen, K. Norrman, F. C. Krebs, *Solar Energy Mater. Solar Cells* **2008**, *92*, 686.
- [2] C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. Jia, S. P. Williams, *Adv. Mater.* **2010**, *22*, 3839.
- [3] M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, F. C. Krebs, *Adv. Mater.* **2012**, *24*, 580.

- [4] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, E. D. Dunlop, *Progress in Photovoltaics: Res. Appl.* **2011**, *19*, 565.
- [5] C. H. Peters, I. T. Sachs-Quintana, J. P. Kastrop, S. Beaupré, M. Leclerc, M. D. McGehee, *Adv. Energy Mater.* **2011**, *1*, 491.
- [6] L. Moro, R. J. Visser, in *Organic Photovoltaics*, Wiley-VCH Verlag GmbH & Co. KGaA, Germany **2009**, p.491.
- [7] G. Dennler, C. Lungenschmied, H. Neugebauer, N. S. Sariciftci, M. Latrèche, G. Czeremuszkin, M. R. Wertheimer, *Thin Solid Films* **2006**, *511–512*, 349.
- [8] S. Chambon, A. Rivaton, J.-L. Gardette, M. Firon, *Solar Energy Mater. Solar Cells* **2007**, *91*, 394.
- [9] S. Chambon, A. Rivaton, J.-L. Gardette, M. Firon, *J. Polym. Sci. A: Polym. Chem.* **2009**, *47*, 6044.
- [10] L. Ma, X. Wang, B. Wang, J. Chen, J. Wang, K. Huang, B. Zhang, Y. Cao, Z. Han, S. Qian, S. Yao, *Chem. Phys.* **2002**, *285*, 85.
- [11] S. Chambon, A. Rivaton, J.-L. Gardette, M. Firon, L. Lutsen, *J. Polym. Sci. A: Polym. Chem.* **2007**, *45*, 317.
- [12] M. Manceau, A. Rivaton, J.-L. Gardette, S. Guillerez, N. Lemaître, *Polym. Degrad. Stability* **2009**, *94*, 898.
- [13] J.-L. Gardette, B. Mailhot, F. Posada, A. Rivaton, C. Wilhelm, *Macromol. Symposia* **1999**, *143*, 95.
- [14] R. D. Scurlock, B. Wang, P. R. Ogilby, J. R. Sheats, R. L. Clough, *J. Am. Chem. Soc.* **1995**, *117*, 10194.
- [15] N. Dam, R. D. Scurlock, B. Wang, L. Ma, M. Sundahl, P. R. Ogilby, *Chem. Mater.* **1999**, *11*, 1302.
- [16] M. Manceau, A. Rivaton, J.-L. Gardette, *Macromol. Rapid Commun.* **2008**, *29*, 1823.
- [17] H. Neugebauer, C. Brabec, J. C. Hummelen, N. S. Sariciftci, *Solar Energy Mater. Solar Cells* **2000**, *61*, 35.
- [18] M. O. Reese, A. M. Nardes, B. L. Rupert, R. E. Larsen, D. C. Olson, M. T. Lloyd, S. E. Shaheen, D. S. Ginley, G. Rumbles, N. Kopidakis, *Adv. Funct. Mater.* **2010**, *20*, 3476.
- [19] Y. Chen, K.-C. Lin, *J. Polym. Sci. A: Polym. Chem.* **1999**, *37*, 2969.
- [20] D. W. Laird, R. Stegamat, M. Daadi, H. Richter, V. Vejins, L. Scott, T. A. Lada, *USA Patent Patent WO 2008/018931A2*, **2010**.
- [21] G. Zhao, Y. He, Y. Li, *Adv. Mater.* **2010**, *22*, 4355.
- [22] F. Deschler, A. De Sio, E. von Hauff, P. Kutka, T. Sauermaann, H.-J. Egelhaaf, J. Hauch, E. Da Como, *Adv. Funct. Mater.* **2012**, *22*, 1461.
- [23] H. Hintz, H. J. Egelhaaf, L. Lüer, J. Hauch, H. Peisert, T. Chassé, *Chem. Mater.* **2011**, *23*, 145.
- [24] M. Manceau, E. Bundgaard, J. E. Carlé, O. Hagemann, M. Helgesen, R. Søndergaard, M. Jørgensen, F. C. Krebs, *J. Mater. Chem.* **2011**, *21*, 4132.
- [25] G. F. Burkhard, E. T. Hoke, M. D. McGehee, *Adv. Mater.* **2010**, *22*, 3293.
- [26] H. J. Egelhaaf, presented at *Photovoltaics at the Nanoscale*, Hasselt, Belgium **2011**.
- [27] A. C. Mayer, M. F. Toney, S. R. Scully, J. Rivnay, C. J. Brabec, M. Scharber, M. Koppe, M. Heaney, I. McCulloch, M. D. McGehee, *Adv. Funct. Mater.* **2009**, *19*, 1173.
- [28] N. C. Cates, R. Gysel, Z. Beiley, C. E. Miller, M. F. Toney, M. Heaney, I. McCulloch, M. D. McGehee, *Nano Lett.* **2009**, *9*, 4153.
- [29] M. A. Faist, T. Kirchartz, W. Gong, R. S. Ashraf, I. McCulloch, J. C. de Mello, N. J. Ekins-Daukes, D. D. C. Bradley, J. Nelson, *J. Am. Chem. Soc.* **2012**, *134*, 685.
- [30] N. C. Miller, S. Sweetnam, E. T. Hoke, R. Gysel, C. E. Miller, J. A. Bartelt, X. Xie, M. F. Toney, M. D. McGehee, *Nano Lett.* **2012**, *12*, 1566.
- [31] J.-M. Zhuo, L.-H. Zhao, R.-Q. Png, L.-Y. Wong, P.-J. Chia, J.-C. Tang, S. Sivaramakrishnan, M. Zhou, E. C. W. Ou, S.-J. Chua, W.-S. Sim, L.-L. Chua, P. K. H. Ho, *Adv. Mater.* **2009**, *21*, 4747.
- [32] T. A. Ford, I. Avilov, D. Beljonne, N. C. Greenham, *Phys. Rev. B* **2005**, *71*, 125212.
- [33] D. Veldman, T. Offermans, J. Sweelssen, M. M. Koetse, S. C. J. Meskers, R. A. J. Janssen, *Thin Solid Films* **2006**, *511–512*, 333.
- [34] D. Veldman, S. C. J. Meskers, R. A. J. Janssen, *Adv. Funct. Mater.* **2009**, *19*, 1939.
- [35] C. Dyer-Smith, L. X. Reynolds, A. Bruno, D. D. C. Bradley, S. A. Haque, J. Nelson, *Adv. Funct. Mater.* **2010**, *20*, 2701.
- [36] A. C. Morteani, R. H. Friend, C. Silva, in *Organic Light Emitting Devices*, Wiley-VCH Verlag GmbH & Co. KGaA, Germany **2006**, 35.
- [37] C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, G. C. Bazan, *Adv. Mater.* **2011**, *23*, 2367.
- [38] A. Kohler, D. Beljonne, *Adv. Funct. Mater.* **2004**, *14*, 11.
- [39] H.-J. Egelhaaf, personal communication, 2011.
- [40] F. C. Krebs, H. Spanggaard, *Chem. Mater.* **2005**, *17*, 5235.
- [41] M. Helgesen, S. A. Gevorgyan, F. C. Krebs, R. A. J. Janssen, *Chem. Mater.* **2009**, *21*, 4669.
- [42] A. Seemann, T. Sauermaann, C. Lungenschmied, O. Armbruster, S. Bauer, H. J. Egelhaaf, J. Hauch, *Solar Energy* **2011**, *85*, 1238.
- [43] Y. X. Liu, M. A. Summers, C. Edder, J. M. J. Fréchet, M. D. McGehee, *Adv. Mater.* **2005**, *17*, 2960.