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# OVERCOMING DEGRADATION IN ORGANIC PHOTOVOLTAICS: ILLUMINATING THE ROLE OF FULLERENE FUNCTIONALIZATION

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## ABSTRACT

Photobleaching rates are investigated for thin films of poly(3-hexylthiophene) (P3HT) blends employing either an indene-$C_{60}$ bisadduct (ICBA) or [6,6]-phenyl-$C_{61}$-butyric acid methyl ester (PCBM) as the electron acceptor. Relative to the bisindene, PCBM significantly enhances resistance to photobleaching of the P3HT donor polymer. We tentatively attribute a decrease in the charge transfer rate as the mechanism responsible for the more rapid photobleaching in the sample containing the bisindene adduct. In order to elucidate the influence of the photobleaching rate on the initial performance of unencapsulated devices, we also monitored the time-dependent behavior for P3HT:fullerene inverted devices. Under conditions of constant illumination, we observe essentially identical behavior in device performance parameters regardless of the energy levels of the electron acceptor. We conclude that over the time frame measured for these devices, the primary degradation mechanism of the active layer is independent of the electron acceptor, despite the enhanced tolerance to photobleaching it may impart to the donor material.

## INTRODUCTION

Recently, several groups have investigated metal oxides, such as $TiO_2$ or ZnO, as an electron transport layer that modifies the effective work function of ITO to render its use as a cathode, thereby inverting the polarity of the device.[1-3] The anode (or hole-collecting electrode) then requires a high work function metal such as Ag or Au by itself or in conjunction with a high work function hole transport layer (HTL) such as poly (3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS). One implication of the inverted device architecture is the low chemical reactivity of the metal oxide layers and environmental stability of high work function top contacts especially in contrast to the Ca/Al alternative. Because of the inherent stability of the constituent layers, this architecture is being used as the basis for scaled-up production of OPV modules. For unencapsulated devices tested in air, the inverted architecture enables lifetimes of several hundred hours compared to <10 hours for conventional devices.[4] Degradation of the low work function top contact represents the single dominant degradation mechanism in OPV devices and further effort is required to understand higher order processes responsible for the inevitable but more gradual decay in performance for inverted devices.

Of particular interest is the nature of the electron accepting molecule and how changes in the energy levels of the frontier orbitals can lead to dramatic changes in photostability of the accompanying electron donor material.

In bulk heterojunction (BHJ) OPV devices, the open-circuit voltage ($V_{OC}$) can be manipulated by changing the energetic offset between the donor material, typically P3HT, and the electron acceptor materials, often a soluble fullerene derivative. By increasing energy level offset between the donor highest occupied molecular orbital (HOMO) and the acceptor lowest unoccupied molecular orbital (LUMO) one can extract a larger $V_{OC}$. Recently, He *et al.* employed an indene-$C_{60}$ bisadduct (ICBA) which, relative to PCBM, shifts the LUMO level 0.17 eV closer to the vacuum level.[5] Optimized devices utilizing ICBA produce a $V_{OC}$ of 840 mV and power conversion efficiencies of 6.5%.[6] Thus far, there have been no studies to link the shift LUMO level to the photostability or device lifetime of bulk heterojunction thin films or OPV devices.
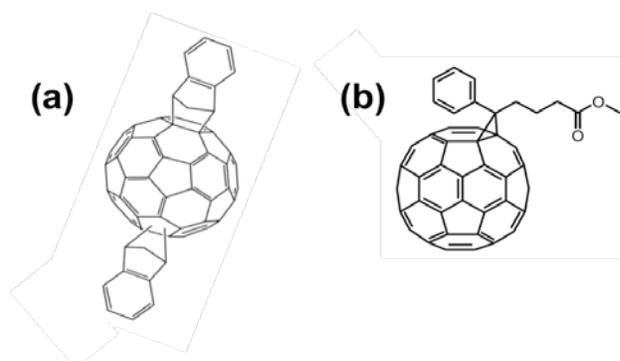


**Figure 1. Molecular structure for (a) indene-$C_{60}$ bisadduct (ICBA) and (b) [6,6]-phenyl-$C_{61}$-butyric acid methyl ester (PCBM).**

This paper compares the photobleaching behavior and the influence of the bleaching rate on early-stage device lifetime for two functionalized fullerene acceptors. For the former, we monitored the change in the absorption spectra over time for P3HT:fullerene BHJ films. Additionally, we continuously monitored the *J-V* performance of unencapsulated inverted devices under constant illumination to investigate the initial performance transients over the course of 200 hours.

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## RESULTS AND DISCUSSION

Figure 2a illustrates the change in UV-Vis absorption for a bare film of P3HT:PCBM as a function of exposure to constant illumination (~100 mW/cm$^2$) for 77 hours. Processing steps for these films were identical to those used for typical inverted device architectures, i.e. 1:1 donor acceptor blending ratio and phase separation formed by a slow dry procedure.[4] Absorption peaks for the initial films are apparent for the P3HT at 515 and 550 nm along with a distinct low energy absorption shoulder at ~610 nm. The latter is known to be associated with interchain interactions in well-ordered domains of P3HT.[7] Successive absorption measurements performed after prolonged illumination indicate a decrease in the height of each absorption peak over time. After 77 hours, the absorption profile exhibits features indicating much of the initial order is present in the aged film, although the fraction of light absorbing chromophores is significantly reduced. It is noteworthy that the higher energy absorption peaks associated with absorption by PCBM show similar behavior in that the peak height decreases but does not vanish over time.
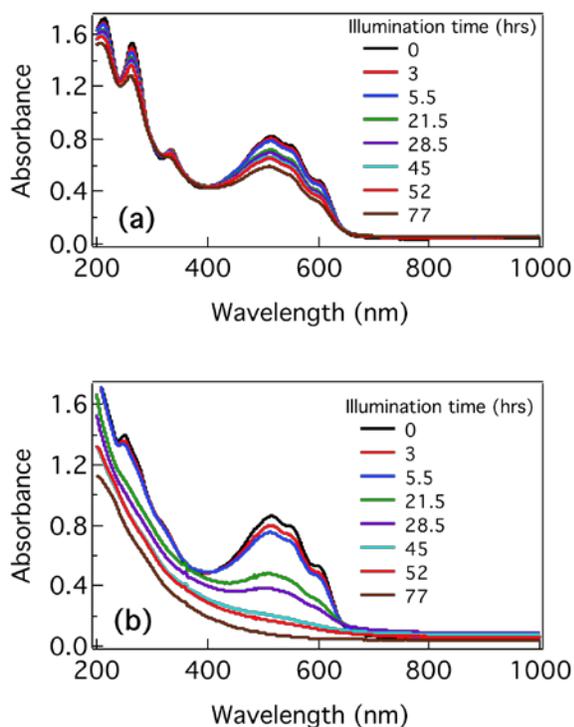




**Figure 2. (a) UV-Vis absorption spectra for thin films of P3HT:PCBM after exposure to continuous illumination (halogen lamp, ca. 100 mW/cm$^2$) in air. (b) Absorption spectra for identically prepared samples utilizing the ICBA acceptor molecule.**

Figure 2b displays the change in absorption for P3HT:ICBA under identical illumination conditions. The initial absorption profile for P3HT is essentially identical for both composite films. The main difference arises after the

sample has been illuminated for more than 5.5 hours, marked by a large drop in the π-π* absorption peaks and near disappearance of the low-energy absorption shoulder. This change in the absorption profile indicates a much more rapid loss in the number of light absorbing chromophores in P3HT and a loss of structural order in the polymer not found in the sample containing PCBM. Likewise, the absorption peak due to ICBA (250 nm) becomes smaller and disappears entirely by 21.5 hours, rendering a broad featureless absorption spectrum for the ICBA component of the film after prolonged illumination.

In polymer:fullerene photovoltaic devices, the polymer component is responsible for the vast majority of absorption in the visible spectrum and thus predominately contributes to photocurrent generation and the power conversion efficiency. To focus on the degradation behavior of the polymer portion of the film, we monitored the decrease in the peak absorption of P3HT, which is located at 515 nm in these films. Fig. 3 shows the linear decrease in the fraction of light absorbed, normalized to the initial value, for the absorption peak as the films are illuminated for 77 hours. The number of light absorbing chromophores is reduced by about 10% in the film containing PCBM, while the absorption in the ICBA decrease approximately 80% in the same period of time (77 hours). Despite similar initial absorption profiles and identical film thickness, heterojunctions formed from PCBM display substantially improved resistance to photobleaching. We were able to reproduce this behavior in subsequent experiments utilizing lower light intensities and P3HT of a higher molecular weight (not shown). However, we note that in the higher molecular weight films, the photobleaching for both types of acceptors occurred at lower rate than reported in Fig. 3.
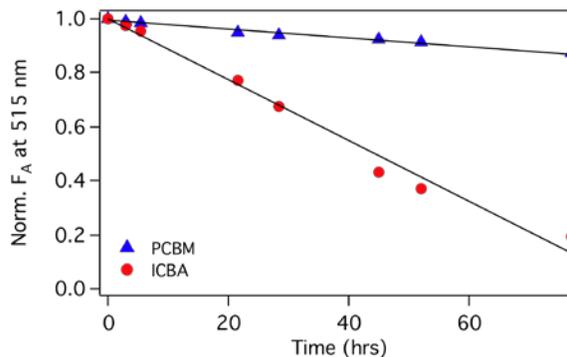


**Figure 3. Normalized fraction of absorbed light at the 515 nm absorption peak for P3HT:PCBM (triangles) and P3HT:ICBA (circles), as a function of light soaking duration. Linear fits to the data are indicated by black lines.**

The literature points to several potential mechanisms responsible for the loss of pi-conjugation and subsequent photoinduced bleaching in P3HT; and consensus has yet to be reached for a single degradation pathway.[8] However, in ambient conditions it has been shown that

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continuous illumination of pristine P3HT results in a linear decrease in the peak absorption of the polymer, and the eventual loss of all light absorbing chromophores. It is well known that an efficient quencher (such as $C_{60}$ or a functionalized fullerene derivative) of the P3HT excited state can be introduced to significantly stabilize P3HT against photobleaching.[9, 10] Tolerance to photobleaching is induced by rapid charge transfer to the acceptor, thereby quenching the reactive photoexcited state residing on P3HT. ICBA clearly functions as an efficient electron acceptor, yielding photovoltaic devices with external quantum efficiency approaching 65%.[6] In Fig. 3, however, linear fits for the photobleaching rate indicate that the bleaching rate for the ICBA sample ($1.1 \times 10^{-2}$ %/hr) is nearly an order of magnitude higher than that of the PCBM stabilized sample ($1.6 \times 10^{-3}$ %/hr). The implication of this significant difference in photobleaching rate suggests differences in the nature of the charge transfer process between P3HT and ICBA. One possible explanation is slower donor/acceptor charge transfer for ICBA relative to PCBM. Although the donor-acceptor charge transfer process may be efficient overall, as evidenced by the high yield EQE, the charge transfer rate may be slower. If this is the case, the P3HT excited state may persist for a sufficient time to react with oxygen in the film, and initiate the photo-oxidation process. PCBM, which is known to quench P3HT on a picosecond time scale[11], will quench P3HT sufficiently fast to prevent appreciable reaction with oxygen. The slower charge transfer step for ICBA is also supported by smaller electron affinity of ICBA, which is responsible for the higher $V_{OC}$ in photovoltaic devices. The smaller electron affinity is responsible for a lower donor/acceptor energetic offset and consequently reduces the driving force for charge transfer. It is likely that this smaller LUMO-LUMO offset will result in a reduction in the rate of the charge transfer process from the polymer to ICBA. Further measurements to directly probe the excited state lifetime of P3HT in P3HT:ICBA heterojunctions are underway in our laboratory.

In order to evaluate the impact of the higher photobleaching rate of P3HT:ICBM on the lifetime of photovoltaic devices, we employed a home-built automated combinatorial light soaking system to monitor performance parameters as a function of illumination. The samples were exposed to constant illumination provided by a sulfur plasma lamp (~70 mW/cm$^2$) in air and *J-V* characteristics were recorded at 30-minute intervals. The change in each photovoltaic parameter over 200 hours is shown in Fig. 4. The $V_{OC}$ and fill factor for the PCBM sample degrades very little (2-5%) over the course of 200 hours, while the short-circuit current density ($J_{SC}$) demonstrates exponential decay. This inverted P3HT:PCBM control cell exhibits typical behavior observed for many devices in our laboratory.[4] As shown in Fig. 4a, the $V_{OC}$ for the ICBA sample increases by approximately 15% over the first 25 hours, which we are not able to explain at this time. Such behavior is typically found in samples where the bare Ag electrodes are used to collect holes due to the increase in work function as the

samples age.[4] In this case, a PEDOT:PSS hole-transport layer is used under the Ag contact, and an initial performance increase is not expected. Furthermore, a concomitant increase in fill factor (Fig. 4b) is not observed for ICBA over the same time period. The $J_{SC}$ for the ICBA sample demonstrates a qualitatively similar decay profile compared to the PCBM device. Overall, in this single comparison of the two acceptor materials, the performance transients are remarkably similar. Additional experiments are needed for complete statistical relevance.
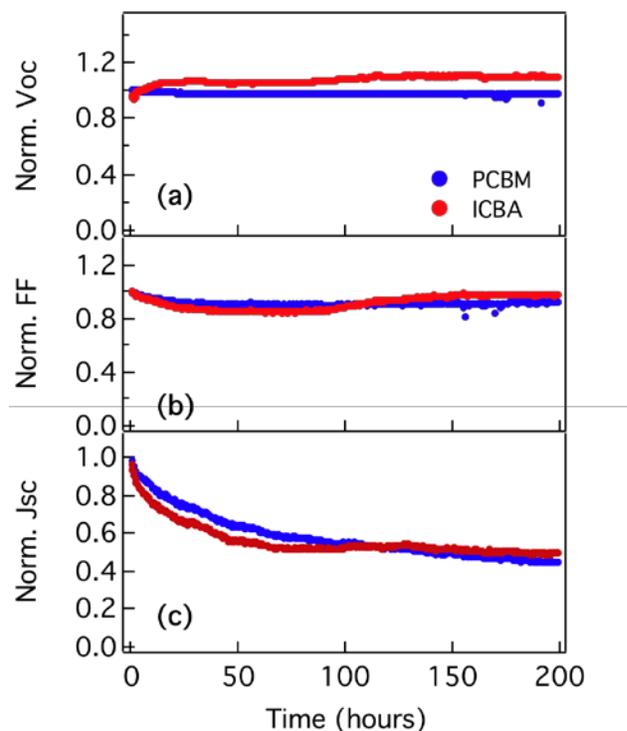


**Figure 4. Performance parameters as a function of illumination time for unencapsulated ITO/ZnO/BHJ/PEDOT:PSS/Ag, where the BHJ layer employs P3HT:PCBM (blue) or P3HT:ICBA (red). Changes are shown for the normalized (a) open-circuit voltage, (b) fill factor, and (c) short-circuit current over the course of 200 hours.**

Bare films (i.e. fee of metal contacts) demonstrate significantly faster photobleaching for BHJs containing the ICBA acceptor molecule. Surprisingly, the same trend is not readily observable in the early stage lifetime behavior in devices with active layers prepared in an identical fashion. It is likely that during the initial stages of operation in unencapsulated devices, oxygen and moisture are effectively blocked from the bulk of the active layer and most of the active area of the OPV device is protected by the PEDOT:PSS/Ag top contact. In that case, regardless of the type of acceptor employed, the BHJ is shielded from the oxidizing effects of the ambient environment and will not photo-degrade.[10] Moreover, we believe that the initial exponential loss in photocurrent

stems from edge-in diffusion, while the end-of-life behavior is determined by ingress through defects in the top contact.[4, 12] Hence, it is likely that the photobleaching bleaching behavior found in thin films represents an additional decay channel that is not primarily responsible for the decay of $J_{SC}$ found in unencapsulated inverted devices.

## CONCLUSION

In summary, the difference in photobleaching rates of P3HT were compared in thin films employing either a bisindene adduct or PCBM as the electron acceptor. Relative to the bisindene, PCBM significantly enhances resistance to photobleaching of the P3HT donor polymer. We tentatively attribute a decrease in the donor-acceptor charge transfer rate for ICBA as the mechanism responsible for the more rapid photobleaching of P3HT. Additionally we monitor the time-dependent behavior for P3HT:fullerene inverted devices to investigate the influence of the photobleaching rate on the initial performance parameters of unencapsulated devices. Under conditions of constant illumination, we observe essentially identical behavior in device performance regardless of the energy levels of the electron acceptor. We conclude that over the timeframe measured for these devices, the primary degradation mechanism in unencapsulated OPV devices is independent of the acceptor-stabilized photobleaching rate of the donor material.

## ACKNOWLEDGMENTS

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