Evidence for Strong and Weak Phenyl-C$_{61}$-Butyric Acid Methyl Ester Photodimer Populations in Organic Solar Cells

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Supporting Information

ABSTRACT: In polymer/fullerene organic solar cells, the photochemical dimerization of phenyl-C$_{61}$-butyric acid methyl ester (PCBM) was reported to have either a beneficial or a detrimental effect on device performance and stability. In this work, we investigate the behavior of such dimers by measuring the temperature dependence of the kinetics of PCBM de-dimerization as a function of prior light intensity and duration. Our data reveal the presence of both “weakly” and “strongly” bound dimers, with higher light intensities preferentially generating the latter. DFT simulations corroborate our experimental findings and suggest a distribution of dimer binding energies, correlated with the orientation of the fullerene tail with respect to the dimer bonds on the cage. These results provide a framework to rationalize the double-edged effects of PCBM dimerization on the stability of organic solar cells.

1. INTRODUCTION

To realize the growing potential of organic solar cells (OSCs), improvements in operational stability remains a key challenge. The development of new polymers and acceptors is continuing to increase the efficiency of OSCs. The current record certified power conversion efficiency is over 17%, achieved in a tandem device architecture incorporating fullerene and nonfullerene electron acceptors. However, the potential loss of OSC power conversion efficiency over time is a key concern for commercialization. This loss can be caused by various stress factors. Environmental elements such oxygen and humidity can react with materials within the device; these factors may be encapsulated against in certain applications, such as those employing glass encapsulation. However, intrinsic factors such as thermal stress, illumination, and interlayer stability cannot be encapsulated against and therefore are always present during operation. In particular, OSCs are often observed to undergo significant light induced degradation during the initial stages of operation. This is termed the “burn-in” and is related to several loss mechanisms which are current areas of interest. Other studies have highlighted the potential for thermally induced degradation of performance, often associated with changes in film morphology. The light induced dimerization of the most widely used, fullerene-based, electron acceptor PCBM (phenyl-C$_{61}$-butyric acid methyl ester) was reported to be a factor in both of these intrinsic degradation pathways, in some cases detrimentally as the underlying cause of device “burn-in”, and in other cases beneficially in improving film morphological stability. In this study, we focus on these apparently contradictory effects of PCBM dimerization and, in particular, provide evidence that light irradiation can result in the formation of two distinct populations of PCBM dimers depending upon the irradiation conditions used (Figure 1).

The dimerization of fullerenes in OSC bulk heterojunctions is known to occur during operating conditions. Beneficial...
effects of PCBM dimerization have been correlated with improved morphology stability in a number of polymer-fullerene systems.\(^{17-19}\) PCBM crystallization and aggregation is one of the key causes of morphological degradation under thermal stress; the formation of the PCBM dimers unit was suggested to impede the nucleation of such PCBM crystallites, thereby enhancing film and device stability.\(^{17}\) The dimer is also immobile compared to the monomer unit.\(^{19}\) However, neutral effects of PCBM dimerization have been observed by Inasaridze et al. within systems of no burn-in despite dimerization occurring and systems with burn-in without dimerization occurring.\(^{20}\) Furthermore, other reports have suggested detrimental effects of PCBM dimerization on the performance and stability of OSCs. Distler et al. reported that dimerization was correlated with the formation of trap states during the degradation of PTDSTzTz:PCBM devices.\(^{15}\) More recently, Heumueller et al. presented further examples of PCBM dimerization causing device degradation in seven different polymer-fullerene material systems.\(^{16}\) From these results, it is clear the effect of fullerene dimerization on stability is nontrivial and the current models in the literature present conflicting conclusions.

The first study of the photochemical dimerization of C\(_{60}\) was reported 20 years ago by Rao et al.\(^{21}\) This 2 + 2 cycloaddition reaction was proposed to be driven by photogenerated fullerene triplet states.\(^{22}\) The dimerization was observed in other fullerenes, such as C\(_{70}\) and PCBM, but at slower rates of formation, attributed to asymmetry and steric hindrance effects.\(^{23,24}\) The topological criteria for dimerization is the alignment of two carbon—carbon double bonds at a separation of less than 4.2 Å. In crystalline PCBM, this requirement is met, with a fullerene cage separation of 3.5 Å. Conversely, PCBM crystallization was reported to lower the yield of long-lived triplet states.\(^{25}\) Temperature dependence studies on C\(_{60}\) show it freely rotates about its center of mass at and above room temperature.\(^{26}\) Although there are many criteria for dimerization, the \(30 \times 30 = 900\) possible orientations have been suggested to aid with the relatively high yields of dimerization in neat C\(_{60}\) films.\(^{27}\) For C\(_{60}\), thermally induced de-dimerization was observed, with an activation energy of 1.25 eV.\(^{28}\) The de-dimerization in PC\(_{60}\)BM dimers was studied by Wong et al.\(^{18}\) The reaction kinetics are found to be very similar to those of C\(_{60}\) with an activation energy of 0.96 eV.

To study the kinetics of PCBM dimerization an absorbance assay was used to probe the fraction of dimers to monomers.\(^{15,16,28}\) This facile assay enables time-resolved monitoring of the PCBM dimerization and de-dimerization. A representative bulk heterojunction of PCDTBT:PCBM thin films was exposed to varying duration and intensity of light exposure followed by dark thermal annealing. By analyzing the kinetics of the thermal de-dimerization, the resulting PCBM dimer enthalpy of dissociation (referred to herein as the dimer binding energy) are correlated with light intensity and duration. This work presents a framework to understand the conflicting effects of PCBM dimerization in OSCs and strategies to maximize both performance and stability.
energetic distribution of dimer binding strengths. Previous studies have probed the yields of de-dimerization using gel permeation chromatography (GPC) or high-performance liquid chromatography (HPLC).\textsuperscript{15,16,18} Time-resolved measurements with these techniques are impractical as they require destruction of the sample and are time intensive to perform. Recently, it was shown that the relative proportions of PCBM monomer and dimer states can be readily assayed from UV/visible absorption spectroscopy.\textsuperscript{15,19} This absorbance assay facilitates collecting time-resolved dimer concentrations, enabling analysis of the kinetics of PCBM dimerization and de-dimerization, as detailed below.

To investigate the de-dimerization kinetics, PCDTBT:PCBM films were initially irradiated with a white light LED (with negligible UV light, see Figure S1 for spectrum) to induce partial PCBM dimerization, and then annealed at 100 °C in the dark to induce de-dimerization. Absorbance spectra were taken periodically while annealing to monitor the kinetics of de-dimerization. Specifically, the change in an absorbance feature at 320 nm was converted to a dimer:monomer ratio using a calibration shown in Figure S2 and reported in more detail elsewhere.\textsuperscript{28} In short, polymer:PCBM films were exposed to a range of irradiances and radiant exposures, and the resulting change in absorbance was calibrated against absolute dimer concentration determined from gel permeation chromatography data. Figure 2 presents a dimer population decay over time following prior irradiation at 186 W m\textsuperscript{-2} for 82 h. Complete reversibility of the photodimerization has previously been shown to occur in this system and is therefore expected to occur here at very long time scales.\textsuperscript{18,26} It was expected that the decay would follow the reaction model described by Eklund and co-workers and used in previous analyses of the de-dimerization kinetics.\textsuperscript{26} This model states the dimer concentration, \(D\), should exhibit a (monoexponential) decay over time upon isothermal annealing, following where
\[
D(t) = D(0) \exp(-kt)
\]
(1)
during where \(D(t)\) denotes the concentration at time \(t\) and \(D(0)\) is the initial dimer concentration. Using this model, Eklund and co-workers were able to precisely fit the thermal transformation of polymeric \(C_{60}\) to monomeric \(C_{60}\) showing the validity of this model for \(C_{60}\).\textsuperscript{22,26}

However, a monoexponential decay does not fit the data in Figure 2. Empirically, we find that a bi-exponential decay describes all data in full:
\[
D(t) = D_{\text{slow}} \exp(-k_{\text{slow}}t) + D_{\text{fast}} \exp(-k_{\text{fast}}t)
\]
where \(D\) is dimer concentration at time \(t\), \(D_{\text{slow}}\) and \(D_{\text{fast}}\) are termed the slow and fast phases, respectively, and \(k_{\text{slow}}\) and \(k_{\text{fast}}\) are the associated decay rate constants, respectively. The biexponential trend is also clearly observed in polystyrene:PCBM films as shown in Figure S3. Several possible interpretations can be considered for this behavior. Fullerenes have been shown to oligomerize,\textsuperscript{21} and the formation of PCBM trimers was reported by several groups;\textsuperscript{18,21} these could contribute to an additional time decay profile. Alternatively, the dimerization process itself could be nonexponential (e.g., described by a stretched exponential) potentially associated with matrix rearrangements required for thermal decomposition to occur; however, we find that a bi-exponential description provides good agreement with experiment (Figure S4). Given that the light spectrum has a broad frequency range, one could conceivably access different reactions and thus dimer pathways depending on incident photon energy; however, no wavelength dependence in dimerization was reported in PCBM films.\textsuperscript{24} Finally, we hypothesize that the intrinsic distribution of relative spatial configurations of PCBM molecules with a film might result in the formation of distinct photodimers, which could then be expected to exhibit different de-dimerization energetic requirements and thus kinetics. Some evidence for dimer complexity is suggested by structured HPLC traces upon light exposure and redissolution.\textsuperscript{16} Next, we experimentally investigate the role of light intensity and time (and thus radiant exposure, or dose) on the de-dimerization time profile to examine this bi-exponential behavior and then report on a theoretical examination of dimer topology.

\textbf{3.2. Reaction Kinetics of Fast and Slow Decays.} The factors determining the ratio of fast to slow phase were investigated by controlling the dimerization illumination conditions prior to annealing. Specifically, three parameters are investigated: the radiant exposure (total energy dose), the irradiance (light intensity), and the duration of the light exposure. First, to probe the effect of radiant exposure, PCDTBT:PCBM films were exposed to a constant 15 kJ m\textsuperscript{-2} from a white light LED array while the irradiance was varied from 63 W m\textsuperscript{-2} to 2155 W m\textsuperscript{-2}. Second, to probe the effect of irradiance, films were illuminated for 50 h with irradiances of 63 W m\textsuperscript{-2} to 2155 W m\textsuperscript{-2}. Lastly, to probe the time dependence, films were exposed to 630 W m\textsuperscript{-2} with a duration of 18 to 14400 min. After, light soaking films were annealed at 100 °C in the dark and absorbance measurements taken intermittently to monitor the de-dimerization. The results of these three conditions are presented in Figure 3a–c. The decay of the dimer population was fitted with eq 1. After fitting with the least-squares error, \(k_{\text{slow}} = 0.135(23) \times 10^{-5}\) s\textsuperscript{-1} and \(k_{\text{fast}} = 9.31(99) \times 10^{-3}\) s\textsuperscript{-1} to one standard deviation for all the decays in Figure 3a–c. As such, we can conclude that the dissociation kinetics of the two separate dimer populations are independent of light irradiation conditions, with differences in overall decay kinetics of the two separate dimer populations being dependent only on variations in the relative magnitudes of the fast and slow de-dimerization phases.

The previously reported rate of de-dimerization in PCDTBT:PCBM was 2.28 \times 10^{-8} s\textsuperscript{-1} which is between the values of the slow and fast dimer kinetics observed here.\textsuperscript{18} The
percentage of slow phase to total dimer \( \frac{D_{\text{slow}}}{D_{\text{slow}} + D_{\text{fast}}} \) is plotted in Figure 3d–f. Figure 3d,e broadly presents the trend that illumination at a higher irradiance causes a greater fraction of slow phase, independent of the radiant exposure or duration of light soaking. In Figure 3f, the fraction of the slow phase is independent of illumination duration. The fraction of the fast to slow phase is therefore dependent on the irradiance of illumination and not the duration of illumination or the radiant exposure. From these measurements, it can be concluded that a key factor controlling the distinct populations is the irradiance. Its underlying mechanism was investigated by analyzing the absolute yield of the slow and fast phases. The amplitude of each decay phase (as calculated from Figure 3) was compared with the light duration and with the radiant exposure. Figure 4a shows that the slow phase correlates with the radiant exposure \( H_r \) and is independent of irradiance. This does not follow the trends observed for the formation of the two-phase kinetics where a dependence on irradiance is observed. Furthermore, the fraction of trimer:dimer is determined from the amplitude of each signal in the GPC. The fraction of PCBM trimer to dimer \( 1:12 \) does not correlate with the fraction of fast to slow phase \( 1:4 \), accounting for reaction stoichiometry. From these observations, it is concluded that PCBM trimerization does not account for the biphase kinetics of decomposition.

### 3.4. PCBM Dimer Configurations

Another potential mechanism resulting in the formation of populations of dimers with different binding energies is the configuration of the PCBM dimer bond. In \( C_{60} \) fullerenes, trimers can form as linear or angled isomers due to variation in bonding location on the cage.\(^{27,29}\) Therefore, it is likely the PCBM dimerization will occur at a variety of bonding locations. The position of the PCBM tail on each of the fullerene units relative to the dimer
double bonds on a C60 cage located at the edge of hexagonal faces of a truncated icosahedron and as such called [6,6] double bonds.21 Aside from the [6,6] double bonds, there are bonds located between a hexagon and pentagon known as [6,5] bonds. These bonds can undergo the 2 + 2 cycloaddition reaction to form fullerene dimers. In C60, a dimer between [6,6]/[6,6] bonds is more stable than the [6,6]/[6,5] bonds or [6,5]/[6,5] bonds by 83 kJ mol⁻¹ and 163 kJ mol⁻¹, respectively.29 Herein, the [6,6] bonds are assumed to be the location of the [2 + 2] cycloaddition in PCBM. The symmetry of C60 means there is no effect of the dimer bond location on the binding energy, consistent with the monoeponential de-}

Figure 4. (a) Fraction of the slow decay to total dimerization correlated against prior radiant exposure. This suggests the reaction follows the expected triplet mechanism previously reported for PCBM dimerization. (b) Fraction of the fast decay to total dimerization correlated against prior irradiance exposure time. This suggests that even at the lowest irradiance used (63 W m⁻²) the rate of formation is not limited by the illumination.

Figure 5. GPC measurements of PCDTBT:PCBM films after varied radiant exposure and irradiance. PCBM trimers are observed in PCDTBT:PCBM films which are identified by a shoulder at 17.3 min in the GPC measurements. The inset shows the linear correlation of trimerization with radiant exposure, \( H_a \). The red traces have similar radiant exposure (≈550 kJ m⁻²) with irradiances from 0.1 kW m⁻² to 1.8 kW m⁻² and all form approximately the same concentration of dimer; therefore, the trimer formation is independent of the irradiance, \( E_\text{ir} \). This is different to the trend observed between the strong and weak dimer \( (E_\text{ir} \text{dependence}) \); thus, the different dimers are not dimer and trimer formation.

bond location will affect the binding strength. There are 30 double bonds on a C60 cage located at the edge of hexagonal...
Figure 6. DFT calculations of the possible PCBM dimer configurations. (a) Dimerization sites occur at double bonds between hexagonal faces. There are eight classes of equivalent distance from the PCBM tail unit. (b) PCBM dimer binding energy dependence on the class on each fullerene; namely, $\beta_{A}$ and $\beta_{B}$. Each ring represents a different DFT calculation noting that for each $\beta_{A}$/$\beta_{B}$ point there are 16 orientations due to the asymmetry of the side group (examples are in Figure S8). Both the size and the color of each ring represent the binding energy relative the $\beta_{A}$/$\beta_{B}$ 8 configuration. (c) Histogram of the binding energies of all possible dimer configurations. The $\beta_{A}$/$\beta_{B}$ = 4 dimers are the most stable, and the spread is not as significant compared to the class, $\beta$. Thus, the class ($\beta$) is a greater factor than the orientation of the PCBM tail of each fullerene.

The histogram of all configurations where $\beta \geq 4$ is presented in Figure 6c. The range of energies is >0.1 eV and, therefore, significant within the range of temperatures used in this study.

The correlation between the class, $\beta$, and binding energy is considered to understand the origins of the distribution in dimer binding energies. In Figure 6c, bonds at $\beta = 4$ and $\beta = 6$ are more stable, and specifically $\beta_{A}$/$\beta_{B}$ = 4:4 is the most stable. Surprisingly, class eight is not as stable. When dimer bonds are formed with the fullerenes cage it distorts the sphere. The distortion and strain are minimized. At bond positions where $\beta = 4$ both the steric hindrance of the side chain is minimized and the distortion of the fullerene cage is minimized.

Inspection of the energy landscape for dimer formation suggests that configurations at class $\beta = 4$ and 6 yield the lowest energies and that substitutions near the fullerene tail are energetically unfavorable and thus unlikely to occur. We tentatively assign the bi-exponential behavior observed experimentally with two configuration classes, combining DFT estimates and relative topological dimerization requirements between PCBM molecules. Excluding sites 1–3 adjacent to the tail, we hypothesize that two populations comprise sites around the equatorial plane (most favorable energetically) and those near the antipode of the tail. It is thus likely that the activation energy assigned to PCBM dimer thermal decomposition, previously estimated as 0.96 eV, is a weighted average $\langle E_{a} \rangle$ of the site distribution revealed in the present work. Given the DFT energy range computed as approximately $\Delta E_{a} \approx 0.10$ eV and our experimental decay rates, we estimate that the two populations exhibit $E_{a,low} \approx 0.9$ eV and $E_{a,high} \approx 1$ eV, compatible with our observations.

To determine the dominating factor of bond stability the variation of binding energies between classes (i.e., $\beta_{A}$/$\beta_{B}$ = 4:4, 4:5, 4:6, etc.) is compared to the variation of binding energies between the same class, but at different orientations (i.e., $\beta_{A}$/$\beta_{B}$ = 4:4, 4:5, 4:6, etc.). The most stable class, $\beta = 4$, has greater variability still as two bonds are perpendicular and two parallel, with respect to the PCBM tail. Six configurations of $\beta_{A}$/$\beta_{B}$ = 4:4 dimers are simulated in Figure S8. The binding energies of these are highlighted in the histogram in Figure 6c and given in Table S1. Although the dimers are topologically very different, the effect on binding energy is less significant. This is not unexpected as changing the bonding orientation might have little effect on the strain experienced by the cage. From these results the dimer bonding position relative to the PCBM tail, $\beta$, is the dominant factor in determining the binding energy of the dimer. In addition, the formation energy of dimer 8.8 was calculated to be +28 meV, which is less stable than the dimer formation set to a reference value of zero. This can be explained considering that, on the other hand some of the fullerenes aromaticity is lost, and since these are antagonist effects it explains the positive energy of formation required. To gain insight into this apparent anomaly, aromaticity analysis was performed. The NICS(0) indexes of the rings involved in the bond creations became strongly antiaromatic. In detail, from values of −2.90 and −2.97 for a single PCBM to values of +3.77 and 5.96 for position 8 (negative values mean aromaticity, positive antiaromaticity). This antiaromaticity lost sheds light into the positive formation energy obtained for position 8.8.

Finally, to understand the effect of PCBM dimer configuration on device performance the variations on frontier molecular orbitals (FMO) are considered. Figure 7 reports the HOMO and the LUMO energy values compared to the dimer binding energy of formation. The HOMO and LUMO energies of the PCBM molecule calculated with these simulation conditions, at −5.57 eV and −3.00 eV, respectively, are considered as a reference. The lines are least-squares error fits to the data. As for the previous analysis, a strong correlation is obtained between the bonds formation energy and the FMO energy. A stabilization of the HOMO and LUMO with greater dimer binding energy was found. This is directly related to the fact that the higher the stability of a molecule, the deeper the
mechanism in C60 by Eklund and co-workers and bi-excited dimerization reaction has been reported as a mono-excited edge. As for understanding, it is possible to comprehend the double-edged e approximately equal to the PCBM monomer. With this weakly bound dimers are formed which have a LUMO level of polarons through PCBM. At lower light intensities greater than 3 kT greater than that of PCBM and as such e formed. These dimers are calculated to have a LUMO level 2-explicitly.


electronic levels of the HOMO, which corresponds to a gain in electronic energy. From these results, it is concluded that the dimer binding energy will affect the electronic properties of PCBM.

4. DISCUSSION

Previous studies have shown PCBM dimerization to be correlated with both beneficial and detrimental effects on stability. Typically, studies presenting the preferential effect of PCBM dimerization are performed at low light irradiance (≈0.1 Sun). However, studies demonstrating the degradation induced by dimerization are performed at higher light irradiance (≈1 Sun). Here it is shown that the irradiance affects the formation of the dimer configuration and, subsequently, the molecular orbital levels. At high light intensities, a larger proportion of strongly bound dimers are formed. These dimers are calculated to have a LUMO level 2–3 kT greater than that of PCBM and as such effect the mobility of polarons through PCBM. At lower light intensities greater weakly bound dimers are formed which have a LUMO level approximately equal to the PCBM monomer. With this understanding, it is possible to comprehend the double-edged effects of dimerization.

The photophysics and irradiance dependence of the dimerization reaction has been reported as a mono-excited mechanism in C60 by Eklund and co-workers and bi-excited mechanism in PCBM by Edman and co-workers. Here, we investigate the irradiance and radiant exposure of PCBM dimerization as a mechanism to probe the effect on the formation of strong and weak dimers. In Figure 3a, after irradiance varying nearly 2 orders of magnitude, we find the extent of dimerization varies by ±8%. Although these values do not support the biexcited model, it does raise an interesting point regarding the slight irradiance dependence on the extent of dimerization which is likely correlated with dimer configurations reported in this paper.

The formation of the de-dimerization fast- and slow-phases have different photophysical mechanisms. The fast phase of weakly bound dimers was time-dependent while the slow phase of strongly bound dimers was irradiance dependent. This is likely due to the matrix constraining the orientation of the weak dimers such that the correct alignment occurs infrequently. Interpreting the formation of strong and weak dimers with these mechanisms allows for the comprehension of the irradiance dependence of dimerization. At higher irradiance, dimers are saturated in the strong configuration before weak dimers are formed, while at lower irradiance, dimers are able to form in both weak and strong configurations. The different factors limiting the weak and the strong dimerization results in an irradiance dependence of formation.

The dominant PCBM dimerization mechanism during the operation of a solar cell will be greatly affected by the location. To predict the overall beneficial or detrimental effects of dimerization it is important to consider the diurnal and annual irradiance variation. A solar cell is likely to exhibit the greatest thermal stress while at high light intensities. The beneficial effects of morphological stability under thermal stress will only be experienced under high light intensity resulting in strongly bound dimers. Additionally, the cyclic conditions will result in the equilibrium tending toward the most stable strongly bound dimer. Therefore, under operating conditions of a solar cell it may be unavoidable not to form the detrimental strongly bound dimers that have been associated with “burn-in”.

5. CONCLUSIONS

This work rationalizes the reasons for the double-edged effects of PCBM dimerization previously reported in the literature. By investigating the de-dimerization kinetics upon thermal annealing two populations of dimers have been found to form. Photodimerization at high irradiance is shown to result in strongly bound dimers, while at lower irradiance weakly bound dimers are also formed. DFT calculations suggest the origin of this energetic distribution in dimer binding energy originates in the location of the PCBM tail with respect to the dimer bonds on the fullerene cage. The simulations also show the dimer binding energy is correlated with molecular orbital levels. The ideas presented enable a pathway to comprehend the varied effects of PCBM dimerization on device stability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.8b05194.

Details on the LED spectrum, dimerization calibration, bi-exponential fitting, stong/weak dimer irradiance dependence, dimer bonding locations, DFT calculations of dimer strain, and additional DFT simulations on PCBM dimer configurations (PDF)

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Figure 7. Effect of PCBM dimerization on the frontier molecular orbital levels as calculated by DFT simulations. The stabilization of the dimer binding energy results in the widening of the band gap. Dimerization results in the increased disorder of both the HOMO and the LUMO level. The solid lines present fits with the least-squares error.


