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Effect of Charge-Transfer State Energy on Charge Generation Efficiency via Singlet Fission in Pentacene–Fullerene Solar Cells

Robin E. M. Willems,† Stefan C. J. Meskers,‡ Martijn M. Wienk,‡ and René A. J. Janssen†,‡,*

1Molecular Materials and Nanosystems and Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
2Dutch Institute for Fundamental Energy Research, De Zaale 20, 5612 AJ Eindhoven, The Netherlands

Supporting Information

ABSTRACT: Singlet fission in pentacene creates two triplet excitons per absorbed photon. In a solar cell, each triplet can generate an electron–hole pair, and hence, external quantum efficiencies exceeding 100% have been reported for pentacene–fullerene solar cells. The energetics of this process are intriguing because the minimum photon energy loss, defined as the energy difference between the (triplet) exciton state and the open-circuit voltage, is less than 0.5 eV and distinctively smaller than that in most organic donor–acceptor solar cells. To investigate the energetics of this process, we analyze the effect of the energy of the lowest unoccupied molecular orbital (LUMO) for different fullerene derivatives. With the LUMO energy becoming lower, the open-circuit voltage increases and charge generation decreases. For all but one of the fullerenes tested, the charge-transfer state energy is distinctively higher than the pentacene triplet energy, revealing that charge generation via singlet fission is actually endergonic. An elementary Marcus model for the rate of electron transfer provides a qualitative description of the experimental trends, in accordance with an endergonic charge transfer. Considering that charge generation from triplet states is endergonic, involvement of pentacene singlet states, either from direct photoexcitation or via triplet–triplet annihilation, cannot be excluded.

1. INTRODUCTION

Singlet fission is a spin-allowed process in which a singlet exciton (S₁) generates two triplet excitons (T₁), dividing the excited state energy over two molecules. Singlet fission was first observed in anthracene crystals, but has since been identified in a wide range of organic compounds. Singlet fission is generally considered to take place via an intermediate correlated triplet-pair state with an overall singlet character (1(TT)), which dissociates into a two independent triplet excitons, according to the following reaction:

\[ S_0 + S_1 \rightarrow 1(TT) \rightarrow T_1 + T_1 \]  

One prerequisite for singlet fission is that the S₁ state energy is at least equal to twice the T₁ state energy (\(E(S_1) \geq 2E(T_1)\)), although endothermic singlet fission has been observed in tetracene, likely by thermal activation of the 1(TT) state. Singlet fission has been studied in detail using ultrafast spectroscopies and is known to occur on extremely short time scales with very high efficiency. By generating two triplet excitons, singlet fission has the potential to generate up to two electron–hole pairs per absorbed photon and double the photocurrent in solar cells, provided the formed triplet excitons can produce free charges. Presently, pentacene/C₆₀ is the most widely studied donor–acceptor combination to exploit the benefits of singlet fission in solar cells. Pentacene has a S₁ energy of 1.83 eV and a T₁ energy of 0.86 eV. In pentacene/C₆₀ solar cells, the external quantum efficiency (EQE) can exceed 100% and values as high as 126% have evidenced the role of singlet fission in charge generation.

It is important to note that to enhance the power conversion efficiency (PCE) of a solar cell, the singlet-fission material must be combined with a second semiconductor with an optical band gap half of that of the singlet-fission material. In that case, the theoretical detailed balance maximum PCE of a single-junction cell is 41.9%, which is a considerable increase compared to the Shockley–Queisser limit of 33.7% for conventional single-junction solar cells. Despite this attractive prospect, such a device has not yet been demonstrated and there is also no appropriate design for it at present. Probably the most viable route to exploit singlet fission is by using it as a downconverter in front of a small band gap solar cell in which two triplet states, generated by the absorption of a single photon, transfer their energy transfer to a small band gap semiconductor, such as PbS or PbSe.

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Alternatively, a singlet fission cell can be combined with a small band gap solar cell, for example, a Si solar cell, in a tandem configuration.\textsuperscript{39}–\textsuperscript{42} It must be noted, though, that the theoretical maximum of a tandem cell, having one or two singlet-fission subcells, does not exceed that of a normal tandem solar cell.\textsuperscript{18} The prospects of using singlet fission in enhancing the efficiency of photovoltaic devices has been reviewed recently.\textsuperscript{43}

An intriguing, but less-discussed aspect of pentacene/C\textsubscript{60} solar cells is the \( V_{oc} \), which amounts to 0.36 V for the cell with an EQE of 126\%.\textsuperscript{22} Although this may seem moderate on an absolute scale, it is actually large, considering the fact that the energy di

dissociation of the pentacene triplet state may require slight

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Figure 1. Overview of the fullerene derivatives used.

2. EXPERIMENTAL SECTION

All chemicals were obtained from commercial suppliers and used without any further purification.

2.1. Square-Wave Voltammetry. Square-wave voltammetry (SWV) measurements were performed inside a nitrogen-filled glove box using an Autolab PGSTAT30 potentiostat (Ecochemie, The Netherlands), in a three-electrode configuration. For thin film SWV, a fullerene-coated Pt wire electrode, Ag bar, and Ag/AgCl electrode served as the working electrode, counter electrode, and quasi-reference electrode, respectively. The fullerene was deposited on the Pt wire via dip coating in a ca. 4 mg/mL solution in ortho-dichlorobenzene. A 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF\textsubscript{6}) in acetonitrile was used as the electrolyte. For SWV in solution, a Pt disk, Ag bar, and Ag/AgCl electrode served as the working electrode, counter electrode, and quasi-reference electrode, respectively. A 0.1 M solution of TBAPF\textsubscript{6} in ortho-dichlorobenzene was used as the electrolyte. About 100 \( \mu \)L of a ca. 4 mg/mL fullerene solution in ortho-dichlorobenzene was added to 3 mL of the electrolyte solution. All potentials are reported versus the ferrocene/ferrocnen redox couple (Fe/Fe\textsuperscript{3+}), which was used as internal reference.

2.2. Solar Cell Fabrication. To fabricate regular configuration pentacene–fullerene solar cells, patterned indium tin oxide (ITO) substrates (Naranjo Substrates) were
cleaned by ultrasonication in acetone, followed by rubbing with an aqueous solution of sodium dodecylsulfate, ultrasonication in aqueous solution of sodium dodecylsulfate, rinsing with deionized water, and ultrasonication in 2-propanol. Just before spin coating, a 30 min UV-ozone treatment was applied. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate (PEDOT:PSS, Clevios P VP Al 4083, Heraeus) was filtered using a 0.45 μm polyvinyl difluoride (PVDF) filter and spin coated at 4000 rpm for 60 s in air and subsequently annealed in a nitrogen-filled glove box for 20 min at 135 °C. Poly(3-hexylthiophene) (P3HT) (Sigma-Aldrich) was dissolved in chlorobenzene to yield a 4 mg/mL solution by stirring at 60 °C for 20 min. Layers of P3HT were applied by spin coating at 2000 rpm for 60 s, followed by an annealing step at 110 °C for 20 min. Pentacene (20 nm, or 40 nm in combination with C60), C60 (35 nm), bathocuproine (BCP) (15 nm), and Ag (100 nm) were thermally evaporated at a pressure below 7 × 10−7 Torr. Fullerene derivatives other than C60 were spin coated from a warm (40 °C) 6 mg/mL solution in chloroform inside the glove box at 1500 rpm for 60 s, after stirring for at least 30 min at 40 °C.

For the inverted fullerene/pentacene solar cells, patterned ITO substrates were cleaned by ultrasonication as described above. An aqueous ethoxylated polyethylenimine (PEIE) solution was diluted with 2-propanol to yield a 2.25 mg/mL solution by stirring for at least 30 min at 40 °C. The sol–gel consisted of a solution of 0.5 M Zn(CH3COO)2·2H2O (98%, Acros Organics) and 0.5 M ethanolamine in 2-methoxyethanol. The sol–gel ZnO was cast directly on clean ITO substrates by spin coating in ambient air via spin coating at 5000 rpm and annealed at 150 °C for 5 min on a hotplate. Inside a nitrogen-filled glove box, KLOC-6, [60]PCBM, [60]IPB, and ICBA were dissolved in chloroform by stirring for 6 mg/mL for at least 1 h at 40 °C. The layers were spin coated at 1000 rpm for 60 s inside the glove box to yield a layer of ca. 37 nm. C60 (37 nm) and pentacene (50 nm) were thermally evaporated at a pressure below 3 × 10−7 Torr. As top contact, MoO3 (10 nm) and Ag (100 nm) were thermally evaporated at a pressure below 6 × 10−7 Torr.

Layer thicknesses were determined using a Bruker DektakXT stylus profilometer. Atomic force microscopy (AFM) measurements were performed on a Veeco Dimension 3100 microscope in the tapping mode with 1 Hz scan rate and ppp-NCHR-50 tips (Nanosensors).

2.3. Solar Cell Characterization. The current-density–voltage (J–V) characteristics of the solar cells were determined by a current–voltage sweep using a Keithley 2636 source–measurement unit. White light illumination (100 mW/cm²) was provided using a tungsten halogen lamp, with Hoya LB120 daylight and Schott GG385 UV filters between the lamp and sample. EQE measurements were performed using a 50 W Philips Focusline tungsten-halogen lamp, which was modulated using a mechanical chopper, and was passed through an Oriel Cornerstone 130 monochromator. The cell was placed in a nitrogen-filled box, and its response was recorded as voltage from a Stanford Research Systems SR570 preamplifier using a SR830 lock-in amplifier. Light bias was applied using a Thorlabs 530 nm LED at 1 sun intensity, or as close to the 1 sun intensity as possible. As a reference, a calibrated Si cell was used. The current density reported was obtained from integrating the EQE spectrum under 530 nm light bias with the AM1.5G solar spectrum.

Sensitive EQE measurements in the sub-band gap region were performed using an Osmar 64655 HLX 250 W halogen lamp, of which the light was chopped using an Oriel 3502 optical chopper. The light was subsequently passed through a Cornerstone 260 monochromator and appropriate sorting filters. The cell was placed in a nitrogen-filled box and, its response was recorded as voltage from a Stanford Research Systems SR570 preamplifier using a SR830 lock-in amplifier. No extra bias light was applied in the sub-band gap EQE measurements. As a reference, calibrated Si and InGaAs cells were used.

2.4. Optical-Electrical Modeling. Optical simulations using the transfer matrix formalism were performed using Setfos 4 (Fluxim AG) software. In the modeling, we used the wavelength-dependent refractive index and extinction coefficients of each layer in the stack.

3. RESULTS AND DISCUSSION

3.1. LUMO Levels of the Fullerene Derivatives. To determine the reduction potentials of the five different fullerene derivatives, SWV experiments were performed on thin fullerene films on a Pt wire. The normalized SWV reduction waves of these fullerene derivatives are shown in Figure 2a and the onsets listed in Table 1. Although the peaks are sharp and the onsets of reduction are clearly defined for KLOC-6, [60]PCBM, [60]IPB, and ICBA, the voltammogram of C60 shows a broad and ill-defined reduction wave. The likely origin of the atypical reduction wave is C60's strong tendency...
to crystallize, which precludes inlets of cations in the film during the reduction. Compared to the other fullerenes, C$_{60}$ is more crystalline in thin films because it lacks solubilizing side chains. To exclude the effects of film morphology, the reduction potentials of all fullerenes have also been measured in an ortho-dichlorobenzene solution. Figure 2b shows the normalized SWV reduction waves. The difference in the reduction potentials of KLOC-6, C$_{60}$ [60]PCBM, [60]IPB, and ICBA matches previously reported differences in reduction potentials of cyclic voltammetry measurements on these or equivalent fullerene derivatives. Figure S1 (Supporting Information) reveals a linear correlation between $E_{\text{red,film}}$ and $E_{\text{red,calcd}}$ for the fullerene derivatives and results in an estimated value of $E_{\text{red,film}} = -0.85$ V versus Fe/Fe$^+$ for C$_{60}$. The LUMO energies (Table 1) were calculated from $E_{\text{LUMO}} = -4.8 - qE_{\text{red,film}}$ [eV].

### 3.2. Pentacene–Fullerene Solar Cells

Solar cells were fabricated to study the effect of the fullerene LUMO energy on the charge generation in combination with pentacene. Pentacene/C$_{60}$ bilayer devices are commonly studied in a nonshunted regular configuration using ITO and PEDOT:PSS as the bottom contact, P3HT as the triplet blocking layer, and BCP with silver as the top contact. However, the fabrication of nonsunted regular configuration devices was only reproducible for C$_{60}$. The other fullerenes cannot be deposited by thermal evaporation, and spin coating of fullerene solutions on top of P3HT/pentacene resulted in mixing of these three materials, reducing device performance. This problem can be circumvented by using an inverted device configuration and first depositing the fullerene layer from solution, followed by thermal evaporation of the pentacene layer. We tested two inverted configurations with either ITO/ZnO or ITO/PEIE layer as bottom contact and MoO$_3$/Ag as the top contact, achieving similar results. In the remainder, we focus on the inverted ITO/PEIE/fullerene/pentacene cells, which gave more reproducible results and compare these to the regular configuration pentacene/C$_{60}$ solar cells. The results for the ITO/ZnO are collected in the Supporting Information (Table S1).

Table 2 and Figure 3a show the solar cell parameters and the $J$–$V$ characteristics of the regular configuration pentacene/C$_{60}$ and inverted configuration fullerene/pentacene solar cells. The inverted configuration C$_{60}$/pentacene has a higher $V_{\text{oc}}$ and FF than the regular pentacene/C$_{60}$ cell, but the short-circuit current density ($J_{\text{sc}}$) is significantly reduced (Table 2). For the regular configuration, the device characteristics are virtually identical to those recently reported by Ehrler et al. For the inverted configuration however, the $J_{\text{sc}}$ is lower than reported by Ehrler et al. (3.2 vs 5.1 mA/cm$^2$) who used an ITO/ZnO bottom contact, but the $V_{\text{oc}}$ and FF are higher. These differences might be related to the differences in active layer thickness (37 nm C$_{60}$ and 50 nm pentacene used here vs 30 nm C$_{60}$ and 60 nm pentacene in ref 31) that reduce the absorption in the active layer. A further difference is the use of PEIE instead of ZnO in the bottom contact. For ZnO devices, we also observe higher $J_{\text{sc}}$ (and lower $V_{\text{oc}}$ and FF) than with PEIE (Table S1, Supporting Information).

The EQE of the regular and inverted pentacene/C$_{60}$ devices (Figure 3b) reveals that the drop in $J_{\text{sc}}$ is associated with a considerable loss of the contribution of pentacene. In the inverted configuration, the EQE at 670 nm is only 16% compared to 47% for the regular configuration solar cell. Optical modeling on the complete layer stacks for both configurations reveals that in the regular device the absorption at 670 nm is higher by a factor of 1.2 (Figure S2, Supporting Information). As a consequence, the reduction of the EQE at 670 nm by a factor of 3 demonstrates a reduced tendency for charge generation in the inverted cells. The possible reason for this will be discussed below.

For the other fullerenes, the $V_{\text{oc}}$ increases with the increasing (i.e., a less negative) LUMO energy (Table 2) but the current density drops, showing that charge generation becomes more difficult. This is also reflected in the EQE of these solar cells (Figure 3b), where for C$_{60}$ [60]PCBM, [60]IPB, and ICBA, the main difference is a drop in the EQE at 670 nm with increasing $E_{\text{LUMO}}$. The only exception is the cell made with KLOC-6, where the $J_{\text{sc}}$ and EQE are lower than expected based on the $E_{\text{LUMO}}$.

### 3.3. CT States

For a deeper understanding of the role of singlet fission and to determine the CT state energy, sub-band gap EQE spectra of all solar cells were measured. Figure 4 reveals a clear contribution to the EQE at photon energies below 1.6 eV, that is, below the absorption onsets of pentacene or of the fullerene derivatives. These sub-band gap features are assigned to a CT absorption that is dominated by a direct transition of an electron from the HOMO of pentacene to the LUMO of the fullerene.

#### Table 1. SWV Onset Reduction Potentials and LUMO Energies of the Fullerene Derivatives in Film and Solution

<table>
<thead>
<tr>
<th>fullerene</th>
<th>$E_{\text{red,calcd}}$ (V vs Fe/Fe$^+$)</th>
<th>$E_{\text{red,calcd}}$ (V vs Fe/Fe$^+$)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KLOC-6</td>
<td>-0.76</td>
<td>-0.94</td>
<td>-4.04</td>
</tr>
<tr>
<td>C$_{60}$</td>
<td>-0.85</td>
<td>-1.01</td>
<td>-3.95</td>
</tr>
<tr>
<td>[60]PCBM</td>
<td>-0.98</td>
<td>-1.09</td>
<td>-3.82</td>
</tr>
<tr>
<td>[60]IPB</td>
<td>-1.01</td>
<td>-1.14</td>
<td>-3.79</td>
</tr>
<tr>
<td>ICBA</td>
<td>-1.10</td>
<td>-1.25</td>
<td>-3.70</td>
</tr>
</tbody>
</table>

*Estimated from the correlation between $E_{\text{red,film}}$ and $E_{\text{red,calcd}}$ (Figure S1). $E_{\text{LUMO}} = -4.8 - qE_{\text{red,film}}$ [eV].

#### Table 2. Characteristics of Inverted Configuration Fullerene/Pentacene Solar Cells and the Regular Configuration Pentacene/C$_{60}$ Cell

<table>
<thead>
<tr>
<th>fullerene</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>$J_{\text{sc}}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>EQE (%)</th>
<th>$E_{\text{CT}}$ (eV)</th>
<th>$\lambda$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$  (reg.)</td>
<td>0.35</td>
<td>6.59</td>
<td>0.47</td>
<td>1.08</td>
<td>47</td>
<td>0.96 ± 0.02</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td>KLOC-6</td>
<td>0.21</td>
<td>1.50</td>
<td>0.50</td>
<td>0.16</td>
<td>12</td>
<td>0.81 ± 0.03</td>
<td>0.70 ± 0.03</td>
</tr>
<tr>
<td>C$_{60}$  (inv.)</td>
<td>0.44</td>
<td>3.23</td>
<td>0.60</td>
<td>0.86</td>
<td>16</td>
<td>1.07 ± 0.01</td>
<td>0.27 ± 0.01</td>
</tr>
<tr>
<td>[60]PCBM</td>
<td>0.45</td>
<td>2.12</td>
<td>0.60</td>
<td>0.57</td>
<td>13</td>
<td>1.12 ± 0.01</td>
<td>0.25 ± 0.01</td>
</tr>
<tr>
<td>[60]IPB</td>
<td>0.46</td>
<td>1.74</td>
<td>0.60</td>
<td>0.45</td>
<td>11</td>
<td>1.14 ± 0.01</td>
<td>0.26 ± 0.01</td>
</tr>
<tr>
<td>ICBA</td>
<td>0.60</td>
<td>0.53</td>
<td>0.59</td>
<td>0.19</td>
<td>2</td>
<td>1.22 ± 0.02</td>
<td>0.31 ± 0.02</td>
</tr>
</tbody>
</table>

* $J_{\text{sc}}$ from integration of the EQE spectrum with the AM1.5G spectrum. 
* EQE at 670 nm corresponding to the S$_0$ → S$_1$ absorption of pentacene. 
* $E_{\text{CT}}$ and $\lambda$ determined by fitting of eq 1 to the sub-band gap EQE, of which the fits are shown in the Supporting Information.
LUMO of the fullerene. Apart from the KLOC-6/pentacene solar cell, the intensity of the CT band decreases when the LUMO energy becomes less negative. This trend is in agreement with the decreasing EQE for photons absorbed above the optical band gap. The position of the CT band shifts to higher energies, which is consistent with the increase in $V_{oc}$ of the solar cell for less negative fullerene LUMO levels.

The low-energy sides of the spectra, were fitted to

\[ \text{EQE}(E) = \frac{f}{E \sqrt{4\pi kT}} \exp \left(-\frac{(E_{CT} + \lambda - E)^2}{4\lambda kT}\right) \]  

(2)
to extract the CT energy ($E_{CT}$) and reorganization energy ($\lambda$) from the spectra. In eq 2, $k$ is the Boltzmann constant, $E$ is the photon energy, $T$ is the absolute temperature, and $f$ is a parameter that is related to the electronic coupling between the initial ground state and the excited CT state and the optical interference in the layer stack. For the inverted configuration C$_{60}$/pentacene solar cell, the fit to eq 2 is shown in Figure 4. The fits for the other solar cells are shown in Figure S3 (Supporting Information). The resulting values for $E_{CT}$ and $\lambda$ are reported in Table 2.

Comparing the results of the fits of eq 2 to the low-energy EQE shoulder for regular and inverted configuration pentacene/C$_{60}$ solar cells reveals that the increase in $V_{oc}$ from 0.34 to 0.44 V by changing the device configuration is reflected in $E_{CT}$, which increases from 0.96 to 1.07 eV, whereas $\lambda$ remains 0.27 eV. It is common to fit eq 2 to the low photon-energy feature of the EQE spectrum, but this does not exclude that CT states at higher energies can be present. In fact, two different CT states were identified at 0.96 and 1.30 eV for pentacene/C$_{60}$ cells by Brigeman et al. using polarized EQE measurements. The $E_{CT}$ for the regular-configuration pentacene/C$_{60}$ solar cell corresponds to the value reported by Lin et al. Lin et al. demonstrate in their study that $E_{CT}$ depends on the nanomorphology of the pentacene/C$_{60}$

Figure 3. (a) $J$–$V$ characteristics and (b) EQE of the optimized inverted configuration fullerene/pentacene and regular configuration pentacene/C$_{60}$ solar cells under simulated AM1.5G (100 mW/cm$^2$) illumination.

Figure 4. Sub-band gap EQE of the optimized inverted configuration solar cells, for KLOC-6 (grey), C$_{60}$ (red), [60]PCBM (blue), [60]IPB (green), and ICBA (purple). A fit of eq 2 for the pentacene/C$_{60}$ solar cell is shown with the dotted red line. Fits for all solar cells can be found in Figure S3 (Supporting Information).

LUMO of the fullerene. Apart from the KLOC-6/pentacene solar cell, the intensity of the CT band decreases when the LUMO energy becomes less negative. This trend is in agreement with the decreasing EQE for photons absorbed above the optical band gap. The position of the CT band shifts to higher energies, which is consistent with the increase in $V_{oc}$ of the solar cell for less negative fullerene LUMO levels.

The low-energy sides of the spectra, were fitted to

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Figure 5. (a) Dependence of $V_{oc}$ and $E_{CT}$ in fullerene–pentacene bilayer cells on the LUMO energy of the fullerene derivative. (b) State diagram for inverted fullerene/pentacene and the regular pentacene/C$_{60}$ bilayer configuration solar cells, for the different fullerenes. The dotted horizontal line indicates the $T_1$ triplet energy level of pentacene (0.86 eV).
interface and $E_{CT}$ varies in the range of 0.97–1.09 eV depending on the nanomorphology. This may rationalize the difference in $E_{CT}$ between regular and inverted configurations. We have performed AFM experiments on pentacene layers evaporated on P3HT as in the regular cells and on layers of C$_{60}$ and PCBM as in the inverted cells (Figure S4, Supporting Information). In each case, we observe the well-known pentacene terraces that indicate a standing-up phase of the pentacene at the top surface, with the only difference being the size of the lateral domains. In the regular cells, this implies that there will be an edge-on arrangement of pentacene and the C$_{60}$ evaporated on top. In the inverted cells, this is less obvious. For pentacene evaporated on C$_{60}$ first a few monolayers of face-on oriented pentacene are formed, on top of which the remainder of the pentacene grows in the standing-up phase. This would leave a predominant face-on interaction of pentacene with C$_{60}$ at the interface. A recent ultraviolet photoelectron spectroscopy study on the energy alignment at pentacene/C$_{60}$ interfaces reveals that the HOMO–LUMO gap at the interface varies from 0.75 eV for an edge-on arrangement of the molecules to 1.50 eV for a face-on orientation. This explains, indeed, in more detail, why there is a difference between the CT ($E_{CT}$) state energy and the open-circuit voltage ($V_{oc}$) of regular versus inverted pentacene/C$_{60}$ cells.

For the other fullerene derivatives, $E_{CT}$ evolves in an approximately linear fashion with the slope close to −1 with the decreasing $E_{LUMO}$ (Figure 5a). The largest deviation is found for C$_{60}$IPB, for which $E_{LUMO}$ could not be determined directly. The reorganization energy varies in a narrow range from 0.25 to 0.31 eV, consistent with previous studies, except for the cell with the KLOC-6/pentacene active layer, where the subgap EQE feature is considerably wider and the fitted $\lambda$ amounts to 0.70 eV, that is, more than double the $\lambda$ value for the other material combinations. Such high reorganization energy is not expected for an electron delocalized on the C$_{60}$ cage. Although some localization of the electron at the ketolactam unit would result in an increased $\lambda$, the broadening of the CT band of KLOC-6/pentacene might have another origin. We note that according to Marcus theory, an increased reorganization energy for the KLOC-6/pentacene combination can result in a reduced rate for charge transfer and hence may explain the low $J_{sc}$ despite the favorable energetics for charge transfer from the pentacene $T_1$ state.

The state energy diagram shown in Figure 5b can be constructed from the data in Table 2. The diagram shows that $E_{CT}$ is strongly correlated with $V_{oc}$. The difference between $E_{CT}$ and $qV_{oc}$ amounts to 0.64 ± 0.03 eV, which is in the usual range for organic solar cells. For KLOC-6, $E_{CT}$ is just below the $T_1$ level of pentacene at 0.86 eV, indicating that charge generation through the triplet state of pentacene is energetically favorable. For C$_{60}$IPB, however, $E_{CT}$ is above the pentacene $T_1$ energy level, which implies that current generation via the pentacene $T_1$ state is endergonic. In particular, although the ICBA/pentacene cell shows the highest $V_{oc}$ and $E_{CT}$, it exhibits a negligible contribution of pentacene (<2%) to the EQE. In their study on pentacene/C$_{60}$ solar cells, Lin et al. rationalize the remarkable result that charge generation is endergonic by the fact that there exists a Gaussian distribution of CT states, such that charge transfer may occur from those CT states that are below the pentacene $T_1$ state. Time-dependent density functional theory applied to C$_{60}$/pentacene clusters has revealed that the conversion from pentacene triplet states to the triplet CT states is in the picosecond regime even though the molecular triplet states are slightly lower than the triplet CT state.

Alternatively, the triplet energy of pentacene may be broadened or even differ from its generally quoted value of 0.86 eV. In fact, only few studies exist in which the pentacene $T_1$ level ($E(T_1)$) has been determined experimentally. Burgos et al. determined $E(T_1)$ at 0.86 ± 0.03 eV in tetracene single crystals from the activation energy for heterofission. Energy electron loss spectra of polycrystalline pentacene films gave a peak at about 0.85 ± 0.05 eV, which was attributed to the lowest pentacene triplet exciton. Time-resolved two-photon photoemission spectroscopy has provided a similar value of 0.87 ± 0.05 eV. In 2-methyltetrahydrofuran, 6,13-bis(trisopropylsilyl),pentacene phosphoresces at about 0.79 eV. On the other hand, using quantum confined PbSe nanocrystals as electron acceptors with tunable acceptor levels, Ehler et al. found that $E(T_1)$ for pentacene lies between 0.85 and 1.00 eV. Using ultrafast optical absorption spectroscopy, Tabachnyk et al. observed resonant triplet energy transfer from pentacene to PbSe nanocrystals with bandgaps of 0.78 and 0.93 eV, but not for crystals with bandgaps of 0.67 and 1.17 eV. Hence, apart from a Gaussian broadening, the exact value of $E(T_1)$ may also differ from the value of 0.86 eV.

In an attempt to correlate the EQE at 670 nm, which represents the pentacene contribution, with the energetics of the electron transfer reaction, we consider the rate of electron transfer $k_{et}$, which is given in the Marcus formalism by

$$k_{et} = \frac{2\pi\langle H_{pp}\rangle^2}{\hbar} \left(\frac{1}{4\pi\kappa kT}\right)^{1/2} \exp\left(-\frac{E_{CT}-E(T_1)+\lambda}{4\kappa kT}\right)$$

Here, $\hbar$ is the Planck constant and $\langle H_{pp}\rangle$ is the electronic coupling between the pentacene $T_1$ state and the pentacene–fullerene CT state. We assume the reorganization energy, $\lambda$, in eqs 2 and 3 to be equal. Although the ground state, triplet excited state, and the CT state may each have a different $\lambda$, it is common to describe an electron transfer reaction with a single (common) $\lambda$. Because eqs 2 and 3 involve the same CT state, the same $\lambda$ can be used in first approximation. Figure 6 shows the correlation between the EQE at 670 nm and the $k_{et}$.
calculated using the $E_{CT}$ and $\lambda$ values from Table 2, assuming that $E(T_1) = 0.86$ eV and $(H_{FP})$ invariant for the various pentacene–fullerene combinations. EQE is the product of efficiencies of absorption ($\eta_A$), singlet fission and subsequent triplet exciton diffusion to the interface. $\eta_{SF-TT}$, charge generation ($\eta_{CG}$), and charge collection ($\eta_{CC}$). The efficiency for charge generation can be expressed as $\eta_{CG} = k_{st}/(k_{st} + k_{et})$, in which $k_{et}$ is the intrinsic decay rate of the triplet states, which is on the order of 6–20 ns in pentacene films. Because $(H_{FP})$ in eq 3 is unknown, a quantitative estimate is not possible. The dashed line in Figure 6 represents a function of the form EQE $\propto k_{st}/(k_{st} + k_{et})$, in which $k_{et}$ represents a small fraction of charges generated from absorption by the fullerenes. We note that apart from differences in charge generation, differences in charge collection $(\eta_{CC})$ may also occur for the different fullerenes. Despite the various approximations, the overall tendency of an increasing EQE at 670 nm with increasing rate constant for electron transfer that appears from Figure 6 demonstrates how changes in $E_{CT}$ affect the efficiency for charge generation. The corresponding graph for a slightly higher (assumed) triplet energy of $(T_1) = 0.96$ eV is shown in Figure S5 (Supporting Information) and reveals a similar, somewhat improved, correlation. The choice for $(T_1) = 0.96$ eV in Figure S5 makes the pentacene triplet state isoenergetic with the pentacene/C$_{60}$ charge transfer state (in the regular device configuration) (Table 2). Equation 3 also provides an indication for the low EQE of the KLOC-6/pentacene cell, where $k_{et}$ is reduced in consequence of the large reorganization energy, despite the exergonic electron transfer reaction, but the EQE is still less than expected based on $k_{et}$ indicating that other effects play a role as well.

We note that the EQE (Figure 3b) also changes in the region where fullerenes absorb more light than pentacene, which is roughly at wavelengths below 500 nm. For the two C$_{60}$ cells, the EQE is larger in this region than for the fullerene derivatives. For the inverted C$_{60}$/pentacene cell, the EQE at 450 nm is higher than at 670 nm. This makes it unlikely that fullerene triplet excitons transfer their energy to pentacene triplets, which then generate charges. Instead, it favors a mechanism in which charge generation originates from the fullerene triplet state at the interface with pentacene. The higher EQEs for the C$_{60}$ cells compared to the other fullerenes may then be caused by the longer triplet exciton diffusion length in C$_{60}$ than in the fullerene derivatives. The fact that the magnitude of the EQE below 500 nm also scales with the fullerene LUMO (except for KLOC-6) matches with the increased free-energy for charge generation, as the energy difference between the fullerene triplet state at 1.5–1.6 eV and the CT state is reduced.

4. CONCLUSIONS

Using five fullerene derivatives, we investigated the effect of the LUMO energy ($E_{LUMO}$) on the performance and energetics of fullerene/pentacene bilayer solar cells. The solar cells showed an increase in $V_{oc}$ and decrease in EQE for less negative $E_{LUMO}$. As expected, the CT state energy ($E_{CT}$) determined from the EQE measurements shows a clear increase with less negative $E_{LUMO}$ of the fullerene acceptor. Both $E_{CT}$ and $qV_{oc}$ increase linearly with increasing $E_{LUMO}$ and the difference is fairly constant at 0.64 ± 0.03 eV. Except for the KLOC-6/pentacene combination, the $E_{CT}$ is higher by at least 0.1 eV than the pentacene triplet state at 0.86 eV. This exhibits that charge generation via singlet fission is endergonic. The decrease in EQE with increasing $E_{CT}$ has been rationalized in semiquantitative way with a Marcus model for electron transfer, which reproduces the trend in the experimental observations fairly well. It also provides a rationale for the KLOC-6/pentacene cell, where the low EQE results in part from large reorganization energy. Although these results are consistent with singlet fission as a mechanism for charge generation, we note that for [60]PCBM and [60]IPB, the EQE for the $S_0 \rightarrow S_1$ absorption of pentacene at 670 nm exceeds 10%, despite the fact that the charge transfer from the $T_1$ state is endergonic by more than 10 times the thermal energy ($kT = 26$ meV). This suggests that for pentacene–fullerene solar cells, not all current must be generated via the pentacene triplet state and might have a singlet state origin, either before singlet fission occurs or via triplet–triplet annihilation.

Our study clearly confirms that even when the CT state in pentacene–fullerene solar cells is above the pentacene triplet state at 0.86 eV, charge generation can be quite efficient. Our study also demonstrates that the energy difference between $E_{CT}$ and $qV_{oc}$ of 0.64 ± 0.03 eV in these cells is not different than expected for an organic donor–acceptor solar cell. The combination of the two results may have intriguing consequences. It suggests that in normal organic donor–acceptor solar cells also, $E_{CT}$ may exceed $(S_1)$ without compromising the EQE. In such cases, higher power conversion efficiencies are possible than hitherto have been considered.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b00568.

Additional information on the correlation of SWV reduction potentials in solution and film, solar cell parameters for ZnO inverted devices, results of optical simulations of the fraction of absorbed photons, subband gap EQE spectra, AFM images, and fits of eq 2 to the experimental data shown in Figure 4, and equivalent of Figure 6, for $E(T_1) = 0.96$ eV (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: r.a.j.janssen@tue.nl.

ORCID

Stefan C. J. Meskers: 0000-0001-9236-591X
René A. J. Janssen: 0000-0002-1920-5124

Notes

The authors declare no competing financial interest.

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REFERENCES


