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

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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 less negative, 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 ($S_1$) generates two triplet excitons ($T_1$), 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 ($1^1(TT)$), which dissociates into a two independent triplet excitons, according to the following reaction:

$$S_0 + S_1 \rightarrow 1^1(TT) \rightarrow T_1 + T_1$$

(1)

One prerequisite for singlet fission is that the $S_1$ state energy is at least equal to twice the $T_1$ state energy ($E(S_1) \geq 2E(T_1)$), although endothermic singlet fission has been observed in tetracene, likely by thermal activation of the $1^1(TT)$ 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/C$_{60}$ is the most widely studied donor–acceptor combination to exploit the benefits of singlet fission in solar cells. Pentacene has a $S_1$ energy of 1.83 eV and a $T_1$ energy of 0.86 eV. In pentacene/C$_{60}$ 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.
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{30,33} 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{35} The prospects of using singlet fission in enhancing the efficiency of photovoltaic devices has been reviewed recently.\textsuperscript{36}

An intriguing, but less-discussed aspect of pentacene/C\textsubscript{60} solar cells is the \( V_{ac} \) which amounts to 0.36 V for the cell with an EQE of 126%.\textsuperscript{32} Although this may seem moderate on an absolute scale, it is actually large, considering the fact that the pentacene triplet energy is at 0.86 eV. For organic solar cells, the minimum photon energy loss, defined as \( E_{\text{loss}} = E_{\lambda} - qV_{ac} \), where \( q \) is the elementary charge, is typically \( \sim 0.6 \) eV.\textsuperscript{32} Although, exceptions to less than 0.5 eV have been reported for conjugated polymers combined with nonfullerene acceptors.\textsuperscript{38}

In this respect, Gao et al. recently emphasized the importance of a consistent and relevant method to determine the optical gap, when comparing the voltage loss as a metric for the performance of organic solar cell materials and argued that the real voltage losses are not much less than 0.6 V in state-of-the-art solar cells.\textsuperscript{39} Nevertheless, the resulting minimum photon energy loss of 0.50 eV in pentacene/C\textsubscript{60} is remarkably small for an organic solar cell with such high EQE.\textsuperscript{37} In fact, the \( V_{ac} \) of pentacene/C\textsubscript{60} solar cells can be even higher. Brigeman et al. report \( V_{ac} = 0.42 \) V.\textsuperscript{40} Even more intriguing, by using graphene as an epitaxial layer to grow pentacene with lying-down orientation, Jo et al. have achieved \( V_{ac} = 0.62 \) V for pentacene/C\textsubscript{60} solar cells.\textsuperscript{41} Compared to the 0.86 eV energy of the T\textsubscript{1} state, the energy loss relative to \( qV_{ac} \) is only 0.24 eV. The EQE of the cells reported by Jo et al. was circa 50% at the pentacene \( S_0 \rightarrow S_1 \) absorption band and, hence, there is no direct proof that singlet fission occurs in this particular solar cell, even though it is very likely.

A potentially useful way of investigating the energetics of charge generation via singlet fission, and consequently via triplet states, is by considering the pentacene/C\textsubscript{60} charge-transfer (CT) state. It is well known that the energy of the CT state (\( E_{CT} \)) in organic solar cells is related to \( V_{ac} \).\textsuperscript{35,36,42} For bilayer pentacene/C\textsubscript{60} solar cells, Lin et al. determined \( E_{CT} = 0.97-0.99 \) eV and \( V_{ac} = 0.28-0.32 \) V,\textsuperscript{43} and proposed that dissociation of the pentacene triplet state may require slight thermal activation.\textsuperscript{44} We note that the energy difference of ca. 0.68 eV between \( E_{CT} \) and \( qV_{ac} \) as found by Lin et al. is slightly higher than the empirical relation, \( qV_{ac} = E_{CT} - 0.6 \) eV, commonly observed for donor–acceptor organic solar cells.\textsuperscript{42} The significant \( V_{ac} \) loss suggests that nonradiative recombination is certainly not strongly suppressed in these cells.

In this work, we study the effect of the energy difference between the triplet energy level of pentacene and the energy of the pentacene–fullerene CT state, using five fullerene derivatives KLOC-6, C\textsubscript{60}, [60]PCBM, [60]PB, and ICBA (Figure 1) with different lowest unoccupied molecular orbital (LUMO) energies (\( E_{\text{LUMO}} \)). Because \( E_{CT} \) is related to the difference in energy between the highest occupied molecular orbital (HOMO) of the pentacene donor and the LUMO of the fullerene acceptor, we can control \( E_{CT} \) via the \( E_{\text{LUMO}} \) of the fullerene. For bilayer fullerene–pentacene solar cells, we observe a clear increase in \( V_{ac} \) which is proportional with a less negative \( E_{\text{LUMO}} \) of the fullerene derivative, with a concomitant loss of EQE associated with the pentacene \( S_0 \rightarrow S_1 \) absorption band. Using EQE measurements, we determine the energy (\( E_{CT} \)) and reorganization energy (\( \lambda \)) of the corresponding CT state. For all but one of the fullerene derivatives tested, \( E_{CT} \) is higher than \( E(T_1) \). This demonstrates that charge generation from the pentacene T\textsubscript{1} state is endergonic. To explain the results in a semiquantitative way, we correlate \( E_{CT} \) and \( \lambda \) in a Marcus model for the rate for electron transfer with the experimental EQE and find qualitative agreement with the experimental trend. Because charge generation from triplet states is strongly endergonic in some cases, contributions from singlet states to the charge generation in pentacene–fullerene solar cells cannot be excluded.

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 threec-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/ferrocenium 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 ultrasonic in acetone, followed by rubbing with an aqueous solution of sodium dodecylsulfate, ultrasonic in aqueous solution of sodium dodecylsulfate, rinsing with demineralized water, and ultrasonic in 2-propanol. Just before spin coating, a 30 min UV−ozone treatment was applied. Poly(3,4-ethylenedioxythiophene):polystyrene 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 polyethyleneimine (PEIE) solution was diluted with 2-propanol to yield a 2.25 mg/mL solution. This solution was spin coated in air at 5000 rpm for 60 s and subsequently annealed for 10 min at 150 °C. Alternatively, ZnO made by a sol−gel route was used. The sol−gel consisted of a solution of 0.5 M Zn(CH3COO)2·2H2O (98%, Acros Organics) and 0.5 M ethanolamine (BCP) (15 nm) was cast directly on clean ITO substrates by ultrasonication in acetone, followed by rubbing with an aqueous solution of sodium dodecylsulfate, ultrasonic in aqueous solution of sodium dodecylsulfate, rinsing with demineralized water, and ultrasonic in 2-propanol. Just before spin coating, a 30 min UV−ozone treatment was applied. Poly(3,4-ethylenedioxythiophene):polystyrene 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.

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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 Focalsun 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 Osram 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 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...
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_{red,fil}(V vs Fc/Fc+</th>
<th>E_{red,fl}(V vs Fc/Fc+)</th>
<th>E_{LUMO}^{b} (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>

*a*Estimated from the correlation between E_{red,fil} and E_{red,fl} (Figure S1). bE_{LUMO} = -4.8 - qE_{red,fil} [eV].

to crystallize, which precludes influx 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. 44 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 derivatives45-47. Figure S1 (Supporting Information) reveals a linear correlation between E_{red,fil} and E_{red,fl} for the fullerene derivatives and results in an estimated value of E_{red,fil} = -0.85 V versus Fc/Fc' for C_{60}. The LUMO energies (Table 1) were calculated from E_{LUMO} = -4.8 - qE_{red,fil} [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 regular device 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 nonsputtered 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 MoO3/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 cell has a higher V_{oc} and FF than the regular pentacene/C_{60} cell, but the short-circuit current density (J_{sc}) is significantly reduced (Table 2). For the regular configuration, the device characteristics are virtually identical to those recently reported by Ehrler et al. 31 For the inverted configuration however, the J_{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_{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_{sc} (and lower V_{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_{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_{oc} increases with the increasing (i.e., a less negative) LUMO energy (Figure 3a) 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_{LUMO}. The only exception is the cell made with KLOC-6, where the J_{sc} and EQE are lower than expected based on the E_{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, which is reflected in an absorption of the CT state at 1.7 eV (Figure 3b).

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_{oc} (V)</th>
<th>J_{sc}^{a} (mA/cm^2)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>EQE^{b} (%)</th>
<th>E_{CT}^{c} (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>0.56</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>

*a*J_{sc} from integration of the EQE spectrum with the AM1.5G spectrum. bEQE at 670 nm corresponding to the S_{0} → S_{1} absorption of pentacene. cE_{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$_{60}$ bilayer...
interface and $E_{\text{CT}}$ varies in the range of 0.97–1.09 eV depending on the nanomorphology. This may rationalize the difference in $E_{\text{CT}}$ 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 C60 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 C60 evaporated on top. In the inverted cells, this is less obvious. For pentacene evaporated on C60, 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 C60 at the interface. A recent ultraviolet photoelectron spectroscopy study on the energy alignment at pentacene/C60 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 ($E_{\text{CT}}$) state energy and the open-circuit voltage ($V_{\text{oc}}$) of regular versus inverted pentacene/C60 cells.

For the other fullerene derivatives, $E_{\text{CT}}$ evolves in an approximately linear fashion with the slope close to −1 with the decreasing $E_{\text{LUMO}}$ (Figure 5a). The largest deviation is found for C60, for which $E_{\text{LUMO}}$ 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 transition broadened or even divided into two subbands (Figure S3, Supporting Information). In each case, we observe the well-known Gaussian distribution of pentacene triplet states, as 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 T1 level ($E(T1)$) has been determined experimentally. Burgos et al. determined $E(T1)$ 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 excitation. Time-resolved two-photon photoemission spectroscopy has provided a similar value of 0.87 ± 0.05 eV. In frozen 2-methyltetrahydrofuran, 6,13-bis(trisopropylsilylthethyl)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 $E(T1)$ 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 $E(T1)$ 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

\[
k_{et} = \frac{2\pi\langle H_{pp}\rangle^2}{\hbar} \left(\frac{1}{4\pi kT}\right)^{1/2} \exp\left[-\frac{(E_{\text{CT}} - E(T1) + \lambda)^2}{4\pi kT}\right]
\]

Here, $\hbar$ is the Planck constant and $\langle H_{pp}\rangle$ is the electronic coupling between the pentacene T1 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 $k_{et}$.

![Figure 6. The EQE at 670 nm corresponding to the $S_0 \rightarrow S_1$ transition of pentacene of fullerene/pentacene solar cells shown in Table 2 as a function of $k_{et}$ calculated from eq 3 using $E(T1) = 0.86$ eV. The dashed line is a guide to the eye and represents EQE at $k_{et}$.](image-url)
calculated using the $E_{\text{CT}}$ and $\lambda$ values from Table 2, assuming that $E(T_1) = 0.86$ eV and $\langle H_{\text{ff}} \rangle$ invariant for the various pentacene–fullerene combinations. EQE is the product of efficiencies of absorption ($\eta_{\text{a}}$), singlet fission and subsequent triplet exciton diffusion to the interface ($\eta_{\text{SS-FF}}$), charge generation ($\eta_{\text{CC}}$), and charge collection ($\eta_{\text{CC}}$). The efficiency for charge generation can be expressed as $\eta_{\text{CC}} = k_{\text{et}}/(k_{\text{et}} + k_{\text{fi}})$, in which $k_{\text{et}}$ is the intrinsic decay rate of the triplet states, which is on the order of $6\text{–}20$ ns in pentacene films.59 Because $(H_{\text{ff}})$ in eq 3 is unknown, a quantitative estimate is not possible. The dashed line in Figure 6 represents a form of the function $\text{EQE} \propto k_{\text{et}}/(k_{\text{et}} + k_{\text{fi}})$, in which $\eta_{\text{et}}$ 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 ($\eta_{\text{CC}}$) 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 $E_{\text{CT}}$ affect the efficiency for charge generation. The corresponding graph for a slightly higher (assumed) triplet energy of $E(T_1) = 0.96$ eV is shown in Figure S5 (Supporting Information) and reveals a similar, somewhat improved, correlation. The choice for $E(T_1) = 0.96$ eV in Figure S5 makes the pentacene triplet state isoelectronic 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 $k_{\text{et}}$ 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 $k_{\text{et}}$ 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 fullerene may then be caused by the longer triplet exciton diffusion length in C$_{60}$ than in the fullerene derivatives.60 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 ($E_{\text{LUMO}}$) on the performance and energetics of fullerene/pentacene bilayer solar cells. The solar cells showed an increase in $V_{\text{oc}}$ and decrease in EQE for less negative $E_{\text{LUMO}}$. As expected, the CT state energy ($E_{\text{CT}}$) determined from the EQE measurements shows a clear increase with less negative $E_{\text{LUMO}}$ of the fullerene acceptor. Both $E_{\text{CT}}$ and $qV_{\text{oc}}$ increase linearly with increasing $E_{\text{LUMO}}$ and the difference is fairly constant at 0.64 ± 0.03 eV. Except for the KLOC-6/pentacene combination, the $E_{\text{CT}}$ 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 $E_{\text{CT}}$ has been rationalized in semi-quantitative 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 ($qkT = 26$ 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 $E_{\text{CT}}$ and $qV_{\text{oc}}$ 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, $E_{\text{CT}}$ may exceed $E(S_1)$ without compromising the EQE. In such cases, higher power conversion efficiencies are possible than hitherto have been considered.

ASSOCIATED CONTENT

S 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)

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Notes

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