

## Electroluminescence from Charge Transfer States in Polymer Solar Cells

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**Abstract:** In this article we report the weak but omnipresent electroluminescence (EL) from several types of organic polymer:fullerene bulk heterojunction solar cells biased in the forward direction. The light emitted from blends of some commonly used polymers and the fullerene molecule is significantly different from that of any of the pure materials comprising the blend. The lower energy of the blend EL is found to correlate with both the voltage onset of emission and the open-circuit voltage of the photovoltaic cell under solar illumination. We accordingly interpret the emission to originate from interfacial charge transfer state recombination and emphasize EL as a very valuable tool to characterize the charge transfer state present in donor/acceptor organic photovoltaic (OPV) cells.

Efforts to increase the efficiency of polymer bulk heterojunction solar cells have already brought several promising examples of the potential of organic materials for power conversion, and a general understanding of their fundamental operational principles is emerging.<sup>1,2</sup> As photovoltaic devices made out of organic materials have the potential to be produced at a pace and price much more beneficial than most solar cells of today, they are considered as promising contenders for future energy conversion. Since these primarily carbon based materials are soluble in organic solvents, they can be deposited by means of ordinary printing techniques at high speed and low cost.

A major limitation for the efficiency of bulk heterojunction solar cells is still found in the various types of recombination events that may occur. Primary exciton recombination, giving rise to polymer luminescence, may occur shortly after photoexcitation if an electron acceptor molecule cannot be encountered within the exciton lifetime. Exciton dissociation sites (donor–acceptor interfaces) have to be encountered within the exciton diffusion length, which for organic PV materials is estimated to range between 4 and 20 nm.<sup>3,4</sup> Polymer excitonic recombination is generally not a limiting factor in most bulk heterojunction cells since an acceptor unit is usually located within this distance, and it has been revealed by exciton emission quenching that almost all created polymer excitons can be dissociated even at a rather low concentration of acceptor

species.<sup>5,6</sup> However, upon transfer of the electron to the acceptor site, and with the hole still left on the polymer, the pair is still affected by Coulombic interactions. If the carriers in this pair are not allowed to diffuse or drift away from each other, recombination of a geminate type will eventually occur anyhow.<sup>7</sup> In particular, if the sizes of the domains of the polymer or fullerene species are too small, the respective charge carriers have no possibility to drift any significant distance and may simply return to its dissociation site origin and geminate recombination will take place. On the other hand, once the carriers are free in thin film blends of fairly high mobility, most of the free carriers do reach the electrodes and free carrier (bimolecular) recombination is not limiting at short circuit and even at the rather weak field corresponding to the maximum power point.<sup>2,8</sup> At open-circuit voltage however, as no charge exits the device, all free carriers must recombine bimolecularly. Thus geminate recombination of the weakly bound electron hole pair must be distinguished from bimolecular recombination of free carriers and is likely one of the most significant limitations for the generation of photocurrent and for efficient energy conversion in several bulk heterojunction solar cells.<sup>9</sup>

The electronic states formed after dissociation of the polymer exciton has been given many names in the literature of organic solar cells in recent years; exciplex, bound electron hole pair,

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bound radical pair, charge transfer state, and charge transfer exciton are probably the most frequently used concepts. Exciplexes are however considered not to originate from ground state interactions, whereas weak ground-state interaction and charge transfer complex formation have been shown to occur in polymer:fullerene blends exhibiting charge generation.<sup>10–13</sup> Photocurrent generation, preceded by direct excitation of the polymer:fullerene charge transfer complexes, has recently been demonstrated with very sensitive EQE measurements.<sup>12</sup> Therefore, we will here refer to this interface bound electron hole pair state as a charge transfer state (CTS). It has been proposed that the significantly weaker binding energy of the created CTS, compared to that of the pristine polymer exciton, must lead to a significantly higher probability of CT state dissociation.<sup>11,13</sup> This second dissociation of the CT state will finally lead to the desired charge separated state (CSS), where the electrons and holes are unaffected by Coulombic interaction from its geminate creator pair and hence completely free from one another.

In organic blends used for light emitting diode applications, the photo- and electroluminescence of the corresponding interfacial state emission has been thoroughly investigated.<sup>14,15</sup> We note that EL through charge pair recombination in such organic solids with two components (molecules or polymers) often shows a similar character of charge transfer states, but typically with a much higher oscillator strength and therefore is more closely connected to the device function of making light. The observation of the weakly bound CT state radiative recombination in polymer PCBM blends used for photovoltaic applications has also recently been made in laser pulsed photoluminescence (PL) studies.<sup>10,11,13</sup> In this case, where the photovoltaic effect is the primary aim, the PL intensity of the CTS recombination is usually very weak, typically orders of magnitude weaker than the pure material PL. It has therefore in many previous PV studies also been completely disregarded. As CTS PL is so weak, the dominating recombination route is therefore expected to occur via other nonradiative routes, such as triplet states.<sup>16</sup>

Photoluminescence (PL) spectra are often measured to determine the efficiency of quenching the emission from direct exciton recombination in donor/acceptor solar cells. The PL emission quenching upon the introduction of acceptor units has frequently been interpreted as demonstrating the ratio of charge generation in bulk heterojunctions but should merely be interpreted as the dissociation efficiency of the polymer exciton. Electroluminescence from photovoltaic polymer/PCBM blends

has at this time and to our knowledge only been evaluated very sparsely.<sup>13,17</sup>

## Results and Discussion

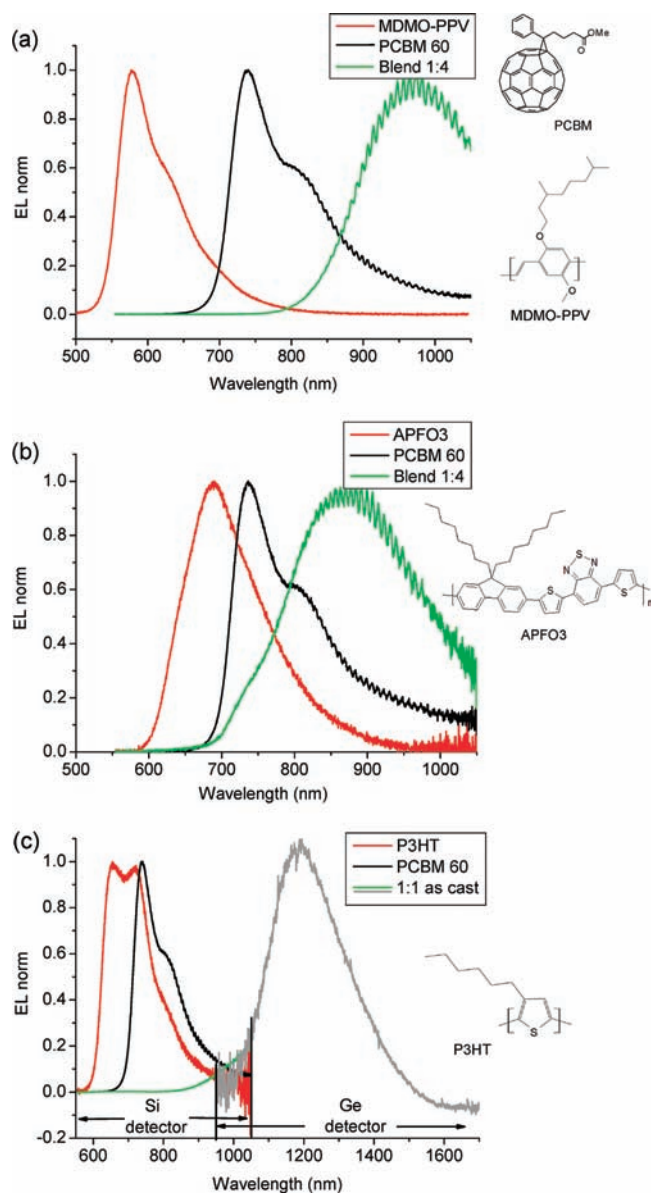
In this paper we study the electroluminescence (EL) created by bimolecular free carrier recombination in polymer:fullerene solar cells and propose EL as an easier way to detect the presence as well as energy of the CT states. As electrons and holes are injected into the device, they must recombine in one way or the other. By populating the available states in the blend, when applying an increasing voltage, it is also easy to correlate at which chemical potential each possible recombination event may occur. The first state that allows for recombination must be the lowest energetic state, and for bulk heterojunctions this is the charge transfer state. Hence it is possible to study only the emission from the low energetic CT state. This is a significant advantage compared to PL experiments, as, in several polymer/PCBM blends, domains of either of the two pure materials are present to some extent and will still give rise to polymer or fullerene PL that may drown the CTS PL signal. Furthermore, by using EL, the detected luminescence signal can be made quite strong and no pumping light is needed, so scattering effects are completely avoided. Although EL by definition must be generated by bimolecular recombination as the carriers are injected into the blend film of the device, the recombination takes place through the same state where both geminate and bimolecular recombination is expected to primarily occur in solar cell operational mode. As explained in the Onsager–Braun model implemented among others by Koster<sup>18</sup> et al., the bound electron hole pair of the CT state allows for a good description of the rates of the two relevant recombination routes. Therefore, forced bimolecular recombination through injection of carriers and generation of EL is suggested to be a good probe of this important state that governs both geminate and bimolecular recombination.

Devices were manufactured by spin coating the active layer blend of different stoichiometry from chloroform or chlorobenzene solutions on top of PEDOT:PSS coated ITO/glass slides. All devices are finalized by thermal sublimation of 0.7 nm LiF and 70 nm Al. The active areas of the cells range from 0.25 to 1 cm<sup>2</sup>. An Oriel optical liquid light guide was located as close to the biased cell as possible and connected to the entrance slit of the spectrometer. A Newton EM-CCD Si array detector cooled to –60 °C in conjunction with a Shamrock sr 303i spectrograph from Andor Tech. served as the emission detection system. The system was wavelength calibrated by an argon lamp to a resolution better than 0.5 nm. The transmission of the entire fiber-monochromator-CDD system was further radiometrically calibrated by an Optronic OL245 M standard spectral irradiance lamp. The CCD detector is “back illuminated” which increases the sensitivity but unfortunately also gives rise to some interference effects at wavelengths between 850 and 1000 nm. For the NIR region a nitrogen cooled Germanium detector (Northcoast EO-817 L) in conjunction with an Oriel 77276 monochromator was utilized. The NIR system was wavelength calibrated but not radiometrically calibrated although the spectral response of the Ge-detector was attended to.

To emphasize the generality of the statements related to charge transfer state luminescence, we have studied a range of

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**Figure 1.** Electroluminescence for the three blends compared to the EL of the pure material comprising the blends. The chosen stoichiometries correspond to the best PV performance.

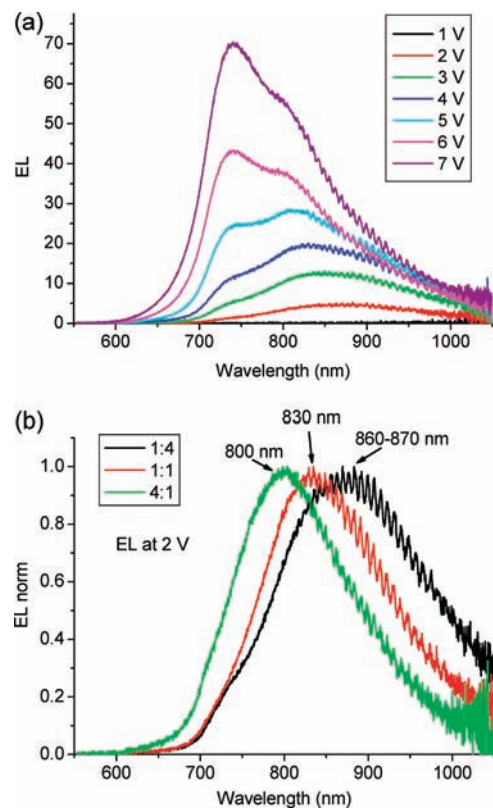
materials of which mainly three are presented in this work. The molecular structures of the selected materials are presented as insets in Figure 1. The commonly used poly(2-methoxy-5-(30,70-dimethyloctyloxy)-*p*-phenylene (MDMO-PPV) is chosen because of its long history in OPV research. The good voltage performing amorphous polyfluorene poly(2,7-(9,9-dioctyl-fluorene)-*alt*-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole) (APFO3) and the crystalline good current deliverer poly(3-hexylthiophene) (P3HT) are further selected. The best performing soluble fullerene molecule Phenyl-C61-butyric acid methyl ester (PCBM) is furthermore included as an acceptor. It is known that this suite of organic polymers displays strong orange, red, and deep red electroluminescence. Most of the EL from the fullerene molecule PCBM is however located outside the visible range, but it is nevertheless rather strong. It should in this context be highlighted that pure PCBM indeed must be a transporter of both electrons *and holes*; otherwise EL in the PCBM device would not be so easy to detect.

When PCBM is blended with any of the polymers, new electroluminescence features however appear. Figure 1 shows the measured EL for the three blend cases, with stoichiometries corresponding to optimal PV performance, together with the EL of the pure material comprising the blend.

As can be seen from all three graphs displaying the normalized EL in Figure 1, a significant EL red shift occurs upon blending the donors and acceptors. It must be noted that the intensity of the red-shifted blend emission generally is lower compared to that from the pure materials but nonetheless very easily detected by our spectrometer systems. In materials where a large difference between the donor-HOMO and the acceptor-LUMO is found, such as in the APFO-3:PCBM case, the emitted light has energies just slightly lower than pure PCBM emission and the peak around 870 nm is hence located within the PCBM tail. A standard material in OPVs for the past decade has been MDMO-PPV. This material blended with PCBM displays the most significant spectral changes possible to detect with an ordinary Si CCD array. In this case the new peak can under no circumstance be interpreted as originating from any of the pure materials. The pronounced CT emission found in MDMO-PPV/PCBM (1:4) and APFO3/PCBM (1:4) blends peak at 970 and 870 nm, respectively. For the P3HT/PCBM (1:1) case the new emission is highly red-shifted and the peak is located outside the detection range of the Si CCD array. A germanium near-infrared detector was therefore used to extend the measuring range for the P3HT blend, and the CT peak is found around 1180 nm. It is from this study hence obvious that new states are present in all three blends. To further elucidate the origin of this emission we also studied the voltage dependence on the EL spectral shape.

Figure 2a displays the EL spectra from a 1:4 APFO3:PCBM blend for different applied voltages. The onset of EL at voltages around 1 V occurs at wavelengths around 870 nm. This emission accordingly corresponds to the lowest energy state available in the blend system but does not correspond to either APFO3 or PCBM and can, as stated above, only be detected in blends of the two materials. At low applied voltages, recombination through the lowest lying charge transfer state is the only possible route. Upon increasing the voltage, a spectral blue shift however occurs. This we attribute to an increasing population of the higher energy states corresponding to the pure materials that accordingly allows for blue-shifted emissive recombination. Similar observations have previously also been reported from polymer/polymer blend LEDs.<sup>15</sup> Recombination and emission through pure PCBM, at wavelengths around 735 nm, occur prior to recombination in the polymer, in all the three material blends. This behavior is also very significant in all OPV blends studied so far. When instead polymer-rich stoichiometries (4:1) are evaluated at high bias, polymer EL in the blend also appears more pronounced than for the presented (1:4) ratio.

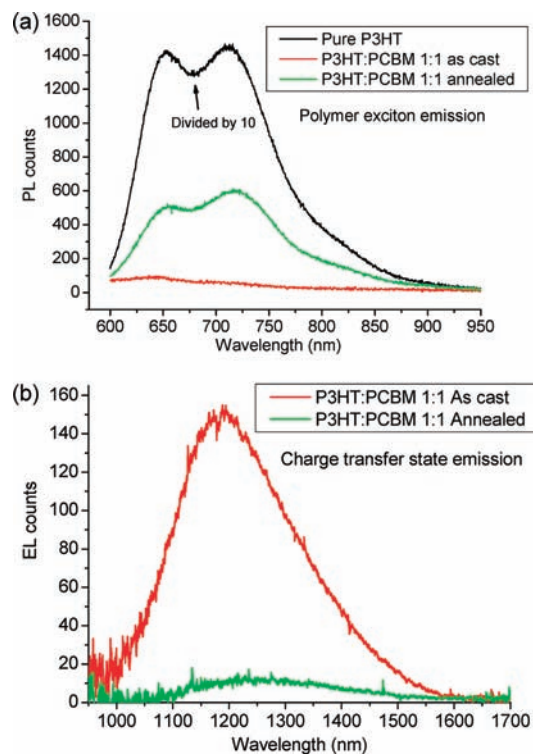
It is further observed that the spectral position of the emission peak of the CT state does depend on the chosen stoichiometry. Figure 2b displays CT EL at a 2 V bias for three different APFO3:PCBM stoichiometries. A pronounced blue shift is observed upon an increase of APFO3 content in the blend, and similar blue shifts were observed also with the MDMO-PPV blend (not presented). At this low bias we assume that we are not generating any excitonic polymer states and only weakly populating the PCBM states. Therefore, the blue shift should not be attributed to an increasing polymer emission tail. A similar observation was made by Veldman et al.<sup>13</sup> studying the CT PL spectra of polyfluorene:PCBM blends comprising



**Figure 2.** (a) EL spectra for the 1:4 APFO3:PCBM system for different applied voltages. (b) Normalized EL spectra at 2 V bias for three different stoichiometries.

different stoichiometries. They attributed the observed blue shift to a decrease in the effective medium dielectric constant upon increasing polymer content. On the other hand, red shifts in organic solid state luminescence are sometimes attributed to clustering and/or crystallization of the organic components. As in the MDMO-PPV:PCBM and APFO3:PCBM blends, the PCBM rather than the polymer is known to show crystallization behavior; we cannot rule out the possibility that the different degrees of PCBM crystallization for the different stoichiometries affect the spectral position of the CT band.

In the P3HT:PCBM blend, where morphological changes can easily be induced as P3HT crystallizes upon annealing of the sample, it is possible to evaluate the morphological effect on both PL and EL emission. It is clearly noted that the annealed P3HT:PCBM cell displays significantly lower CT state EL intensities compared to the as cast film. This is attributed to an actual quenching of radiative CT state emission, as opposed to red shifts taking the emission outside of the detection range. A red shift of the peak of  $\sim 60$ – $70$  nm can also be observed upon annealing. This spectral shift can hence no longer be attributed to a change in the effective medium dielectric constant but rather to molecular clustering. The larger domains of pure crystalline materials formed upon annealing hence not only lower the probability of polymer exciton dissociation, as verified by the PL studies (Figure 3a) where the polymer exciton radiative recombination indeed is enhanced upon annealing, but also apparently lower the electroluminescence through the CT state (Figure 3b). Knowing that annealed P3HT:PCBM devices are superior compared to as cast films when it comes to current extraction in the PV operational mode, it is evident that larger crystalline domains of pure materials formed upon annealing are beneficial, although at the expense of some incomplete polymer exciton

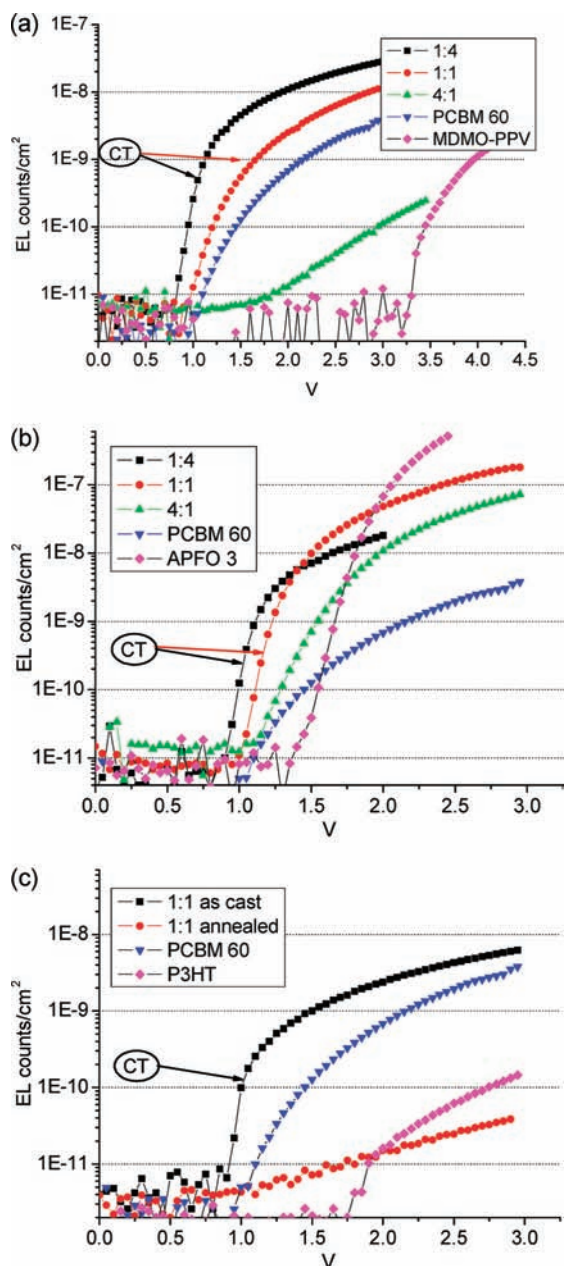


**Figure 3.** (a) PL spectra dominated by polymer exciton recombination from P3HT:PCBM blends before and after annealing compared to the pure material (black) PL. (b) EL spectra dominated by CT state recombination before and after annealing.

dissociation. As similar observations are also made for more amorphous blend components, whose morphology is instead altered by solvent/additive treatments, a general conclusion could be that, for photovoltaic operation, an optimum pure phase size somewhat larger than the exciton diffusion length may actually be beneficial in several cases. As it was further observed that the current in the forward biased annealed devices was similar or larger as compared to the same devices before annealing, the necessary recombination must after annealing hence occur more strongly through nonradiative pathways such as, i.e., triplet states.

Two explanations could account for the observed increased nonradiative recombination current upon annealing. First it is possible that the number of nonradiative pathways is actually increased upon annealing. Second, the increased nonradiative recombination current can also be due to an increased dissociation rate of the CT state. Easy splitting of CT states formed when electron and hole meet each other forces the carriers to take the existing, nonradiative pathways, rather than the radiative pathway through the CT state to recombine. This will increase the nonradiative recombination current as compared to the radiative recombination current. Removing these nonradiative pathways would thus result in more long-lived free carriers than is currently the case. This decreased recombination would be very beneficial for the open-circuit voltage of the devices and accordingly overall efficiency. Identifying the pathways of nonradiative recombination in polymer:fullerene solar cells is therefore a very important subject in the quest for increasing the efficiency of this type of photovoltaic devices.

We further evaluated the light voltage dependence with a setup comprising a large area calibrated Oriel Si photodiode, a Keithley 2400 sourcemeter, and a Keithley 485 picoammeter controlled by a Labview program. This setup allows for



**Figure 4.** Light voltage curves for the MDMO-PPV:PCBM blends (a), APFO3:PCBM blends (b), and (1:1) P3HT:PCBM blend (c). All three graphs display the earlier onset of CT emission.

determining the photon output as a function of applied voltage as well as external quantum efficiencies (EQEs) of the EL, as long as the emission has a higher energy than the band gap of the Si detector. By detecting at what voltage the cell starts to emit light (of any wavelength  $< \sim 1050$  nm) it is again possible to evaluate the energetic impact of the charge transfer state. As the light onset as detected by the Si photodiode corresponds to the product of EL emission and the Si diode detection capability, the actual EL light onset cannot accurately be determined. Differences in the interfacial LiF layer between the different devices, as well as minor thickness variation of the emitting layer, may furthermore to some extent affect the emission onset voltage. It is nevertheless very feasible to observe the large impact of blending donors and acceptors [Figure 4]. It is verified that the onset of emission correlated to the charge transfer state occurs at voltages significantly lower than those

corresponding to pure material EL. Although no direct relation between emission peaks and emission onset can be identified at this point, a clear trend prevails. The curves marked in the graph as “CT” are those whose spectra certainly cannot contain any contribution from either pure polymer or PCBM emission. As the photon energies corresponding to the CT state are lower than those of the polymer and the PCBM, lower potentials are needed to generate a photon flux compared to the case of pure materials. Because electron injection into the LUMO of PCBM and simultaneous hole injection into the HOMO of the polymer are only achievable in the blend, it is in complete accordance with the lower bias needed for EL generation compared to that from any of the two pure materials.

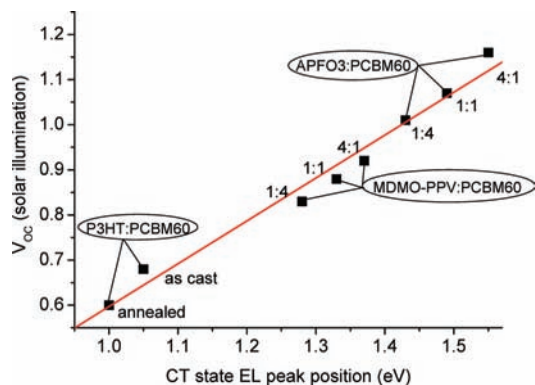
The EQE of the charge transfer state electroluminescence can in addition be obtained from this measurement. The two amorphous polymers APFO3 and MDMO-PPV blended with PCBM displays an efficiency of emission at  $\sim 10^{-6}$  photons/injected electrons. The more red-shifted CT emission of the P3HT:PCBM blend could unfortunately not be accurately evaluated with this Si detector setup. It should therefore also be noted that the shape of the curve corresponding to the 1:1 annealed P3HT:PCBM blend in Figure 4c to a large extent is attributed to the poor detection capability of the detector. It can nevertheless be safely concluded that a dominating part of the injected carriers in all devices does not participate in radiative recombination and, from the Ge detector measurement, that radiative recombination is even further lowered upon P3HT annealing. It is well-known that, for ordinary organic light emitting diodes (OLED) with single materials, spin statistics predict that 25% of the recombination goes through emissive singlet states and 75% through nonradiative triplet states, in the absence of intersystem crossing. Therefore it is plausible with triplet formations also in our bulk heterojunction solar cell, here forward biased and acting as an OLED. Exciplex triplet states formed between donor and acceptors utilized as phosphorescent emitters in white OLEDs<sup>19</sup> as well as efficiency limiting recombination pathways in OPVs<sup>20</sup> have been reported. Because of the measured low EQE, most of the recombination must go through some variant of such nonemissive pathways. A possible route may also be that a large part of the CT states formed upon injection could subsequently couple to even lower pure polymer or PCBM triplet states, which subsequently also recombines nonradiatively.

Although it is important to fully distinguish between forward bias (LED operation) and solar cell operation, we believe that the very important charge transfer state plays a significant and partly similar role under these different operational modes. Under weak field PV operation, the CT state primarily acts as an intermediate state to facilitate polymer exciton dissociation but likely also as an interfacial recombination center for both geminate and free carrier bimolecular recombination. Assuming that the Onsager–Braun theory, frequently deployed<sup>2,18,21</sup> for describing charge transfer and recombination rates in two-component organic solar cells, is a valid description, then both geminate and bimolecular recombination *in blends* may both occur primarily through the CT state. As we have shown here,

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**Figure 5.** Open-circuit voltage from the cells under solar illumination vs the peak position (in eV) of the charge transfer state electroluminescence. Three different stoichiometries for APFO3:PCBM and MDMO-PPV:PCBM as well as annealed and as cast P3HT are included in the graph.

the CT state is involved in bimolecular recombination of injected free carriers, and as the CT state furthermore is the interfacial state where dissociation occurs in PV operation, it is very plausible that the CT state also in this role still provides at least one route for recombination of generated charge carriers.

It has previously been confirmed that the important solar cell parameter of open-circuit voltage ( $V_{oc}$ ) correlates with the oxidation potential of the polymer and accordingly with the energy difference between the HOMO of the donor and the LUMO of the acceptor.<sup>22,23</sup> As this difference is associated to the energy of the CT state, it is rewarding to plot the observed CT emission peak position vs the  $V_{oc}$  under solar illumination of the same cell. The overall observation and correlation with energetics from CT peak emission to the  $V_{oc}$  from the same devices are indeed established and presented in Figure 5. The confirmed linear relation with a slope of 1 and a y-axis offset of  $\sim 0.4$  V hence agrees well with the previous results obtained from oxidation potential measurements as well as those obtained from the weak CT state absorption<sup>12</sup> and photoluminescence<sup>13</sup>

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characterizations. The energy of the blend charge transfer EL is hence found to correlate with the effective single band gap of different bulk heterojunction blends, namely the donor-HOMO and acceptor-LUMO level difference. In addition to that, we can by stoichiometric as well as morphological alterations also demonstrate that the CT state energy is the actual factor that determines the open-circuit voltage and not merely the HOMO–LUMO level difference.

In conclusion, we present evidence for low energy charge transfer states in polymer/PCBM photovoltaic blends, through EL, and note that low voltage EL spectra and light–voltage relationships are very simple and efficient ways to detect CT states and characterize the energetics of the same. A minor part of the interfacial recombination via the CT states is radiative, but this can only constitute a fraction of the total recombination.

Bimolecular radiative recombination of injected carriers in bulk heterojunction solar cells hence appears to be dominated by the preceding formation of CT states. Although the formation of the CT states in the photovoltaic mode is expected to be required to efficiently dissociate the strongly bound polymer exciton, the CT state is unfortunately still in a weakly bound configuration and geminate as well as bimolecular recombination through this state is still allowed. The radiative bimolecular recombination route is proven in this paper, whereas the radiative geminate route is only suggested to occur through the same route. Electroluminescence from a PV cell under forward bias hence probes the states and parts of the mechanisms that are the very same ones that will give rise to non-negligible losses in a PV cell under illumination. The dominating nonradiative recombination routes under forward bias are however still kept in the dark but must be further elucidated in future work.

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