Dominating recombination mechanisms in organic solar cells based on ZnPc and C60

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We investigate the dominating recombination mechanisms in bulk heterojunction solar cells, using a blend of ZnPc and C60 as model system. Analyzing the open-circuit voltage (Voc) as a function of illumination intensity, we find that trap-assisted recombination dominates for low light intensities, whereas at 1 sun, direct/bimolecular recombination becomes important. The recombination parameters are not significantly influenced by the blend mixing ratio and are also valid for injected charges. By changing the hole transport layer, recombination at the contact is separately identified as further mechanism reducing Voc at higher light intensities. © 2013 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4802276]

In the last few years, organic photovoltaics1–5 has made enormous progress. Nevertheless, a significant further increase in efficiency is needed to fully leverage the advantages of this technology. The active region of organic photovoltaics is usually a heterojunction with nanoscale morphology, making it challenging to obtain a microscopic understanding. This is particularly true for recombination, which is the most important intrinsic loss mechanism in solar cells. Recombination sets the equilibrium charge carrier density within the photoactive material by balancing the optical generation at open circuit. The lower the recombination, the higher the charge carrier density at a given illumination intensity and the higher the potential for a high open-circuit voltage Voc.6 The reason is that the electro-chemical potential, which is a representative energy of one charge carrier in an ensemble, increases with charge carrier density. This effect of recombination limiting the open-circuit voltage was experimentally shown for organic solar cells by charge carrier extraction and transient photovoltage decay experiments.7,8

When extracting charge carriers (e.g., at short circuit or the power-generating region of the current-voltage curve), recombination is in competition with the field-dependent extraction of charges and reduces the fill factor and eventually the short circuit current density Jsc, commonly used to determine the order of recombination. However, Jsc is not the most appropriate point of the current-voltage characteristics (J–V curve) to study recombination, as a considerable amount of charges is extracted. This was a matter of discussion in the last years9,10 and focus was turned to Voc.11–14 Open circuit is much more suited to study recombination, especially if the contacts are selective, which means that all charge carriers are forced to recombine within the device at Voc.6

Several studies on different polymer solar cells have identified geminate recombination,15,16 bimolecular recombination,16–20 trap-assisted recombination,9,21–23 monomolecular recombination in general,24 or even a combination of geminate and non-geminate recombination25,26 as loss mechanisms. These results demonstrate the great controversy around this important topic.

In this contribution, we study the dependence of Voc on light intensity examining a large intensity range (10 μW/cm²–1 W/cm²), which allows to clearly distinguish the order of the recombination (monomolecular/trap assisted and bimolecular/direct). Although discussed in literature,12,14 trap-assisted recombination has not yet been identified as distinct recombination mechanism when examining Voc as a function of light intensity. Commonly, only a superposition of direct and trap-assisted recombination was found as reason increasing the slope of Voc as a function of the logarithm of the light intensity. However, due to their distinct dependencies on charge carrier density, a clear transition between the regions where one or the other mechanism dominates is expected, if these are really two separate mechanisms. Additionally, it is not clear where the huge amount of non-radiative recombination27 results from and what role the contacts play. Here, we identify a transition between the two bulk recombination regimes. We separately visualize the influence of recombination at the electrode by using doped charge transport layers with tailored energy levels and work functions. The experimental data are modeled by drift-diffusion simulations including trap-assisted and direct recombination, and the energetics of the contact materials. We show that the results obtained from fitting J–V data under illumination hold for the (dark) injection current in forward direction as well. Consequently, we can quantify the contributions of the three recombination mechanisms as a function of light intensity.

The investigated solar cells are prepared by subsequent deposition of all layers in a vacuum chamber as described in Ref. 28. The stack of all devices reads: ITO/C60:NDI1 (20 nm, 3 wt. %)/ZnPc:C60(50 nm, x:y)/HTL(1 nm)/p-HTL (45 nm, 5 wt. %)/p-dopant(2 nm)/Al(100 nm). Here, HTL means hole transport layer, where DI-NPD (N,N-diphenyl-N,N-bis(4-(N,N-bis(naphth-1-yl)-amino)-biphenyl-4-yl)-benzidine, ionization potential (IP) of 5.3 eV) and MeO-TPD (N4, N4’, N4”-tetrakis(4-methoxyphenyl)-1,1’-biphenyl)-4,4’-diamine, IP = 5.1 eV) are applied. The p-dopant is NDP9 in

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case of Di-NPD and NDP2 in case of MeO-TPD. NDN1 is an n-dopant. Details on the materials can be found in Ref. 28. Current-voltage characteristics are recorded under simulated sunlight (16 S-002 Solar Light Company Inc., Glenaside USA). The intensity is measured by a calibrated silicon reference diode (Hamamatsu, S1337-33BQ) and adjusted by using neutral-density filters and by varying the distance between the specimen and the fiber coupled to the sun simulator.

Simulated J-V curves are obtained by drift-diffusion simulations29 of the three-layer solar cell stack (n-C60/blend/p-HTL) assuming a realistic doping concentration (5 × 10^{19} cm^{-3}) in the doped layers as boundary condition. Knowing the exact value is not required as the simulation results are independent of the doping concentration as long as the doped layers are highly conductive compared to the blend.31 This is the case as a variation of the HTL thickness does not change the devices’ series resistance.28 Charge carrier mobilities are chosen to match the overall shape of the J-V curve (see Refs. 28 and 30), the dielectric constant is set to 4.9, which is close to impedance measurement data,32 and the absorption profile is obtained from optical modeling (Details in Ref. 28). Regarding the discussion of $V_{oc}$, only the effective donor-acceptor gap $E^D_g = \Phi_{donor} - \Phi_{acceptor}$ (EA is electron affinity), the effective densities of states, and the prevailing recombination mechanisms and their parameters are important. The strategy applied to find these parameters will be discussed later. Here, we review analytical approaches to $V_{oc}$ as a function of light intensity in case of selective contacts and a spatially constant generation rate.

We start with the equation for $V_{oc}$, which directly results from the quasi-Fermi level splitting with the assumption of relaxed electron and hole states:6,33

$$eV_{oc} = E^D_g - k_BT \ln \frac{N_C N_V}{n p}$$

(1)

with $n$ and $p$ as electron and hole densities and $N_C$ and $N_V$ as effective densities of states. To adjust this classical semiconductor equation to disordered organic solids, additional parameters might be added, and the $N_C N_V$ replaced.34 If recombination happens via charge-transfer (CT) states, and the prevailing recombination mechanisms and their parameters are important. The strategy applied to find these parameters will be discussed later. Here, we review analytical approaches to $V_{oc}$ as a function of light intensity in case of selective contacts and a spatially constant generation rate.

The expression $np$ in Eq. (1) can be replaced by applying the approach of Ref. 6: Assuming selective contacts, the recombination rate $R$ equals the generation rate $G$ at $V_{oc}$. Thus, Eq. (1) can be rewritten for direct (bimolecular) recombination with $R_d = \beta n p = \beta G$,

$$eV_{oc} = E^D_g - k_BT \ln \frac{N_C N_V}{G \beta}$$

$$= E^D_g - k_BT \ln \frac{N_C N_V}{1 \text{m}^3 \text{s}^{-1}} + k_BT \ln \frac{G}{1 \text{m}^3 \text{s}^{-1}}.$$

(2)

This equation predicts that $V_{oc}$ scales logarithmically with the illumination intensity because $G$ is proportional to the incoming photon flux. The slope in a graph, where the illumination intensity is plotted in the logarithm to the base 10, is $k_T / \log(\exp(1)) \approx 2.3 \times k_BT \approx 59 \text{mV/decade} (T = 300 \text{K})$.

In case of indirect/trap-assisted recombination, $R$ can be expressed by the Shockley-Read-Hall (SRH) theory, which gives in the simplest case $R_{SRH} \approx cN_{t} n_{p} / N_{t} n_{p}$, where $c$ is the capture rate and $N_{t}$ the concentration of traps. We combine both parameters in one coefficient $k_{SRH} = cN_{t}$. If the majority of the present charge carriers is photogenerated (i.e., $n_{p} = p_{ph}$), this equation can be simplified to $R \approx k_{SRH} N_{t} p_{ph} / 2 = k_{SRH} N_{t} p_{ph} / 2$. Thus, $G \propto p_{ph}$. This proportionality is also valid close to the contacts, where a high background density $(n_{d}, p_{d})$ of one charge carrier species may exist due to low injection barriers, e.g., $n_{d} \gg n_{ph} \gg p_{ph} \gg p_{d} \rightarrow R \approx k_{SRH} N_{t} p_{ph}$. Setting $R = G$ and replacing $np$ in Eq. (1) yields the SRH case

$$eV_{oc} = E^D_g - k_BT \ln \frac{N_C N_V}{G^2 \beta}$$

$$= E^D_g - k_BT \ln \frac{N_C N_V}{1 \text{m}^3 \text{s}^{-1}} + 2k_BT \ln \frac{G}{1 \text{m}^3 \text{s}^{-1}}. \quad (3)$$

Here, $C$ is a parameter containing $k_{SRH}$. The slope of $V_{oc}$ plotted as a function of the common logarithm of $G$ is $2.3 \times 2k_BT$. This value is twice the slope of $V_{oc}$ for direct recombination. Therefore, the slope of $V_{oc}$ as a function of the logarithm of the light intensity can be used to distinguish between both recombination mechanisms. This idea was discussed in a similar derivation for amorphous silicon devices in Ref. 37 and planar heterojunction organic solar cells in Ref. 38. It has also been applied several times when discussing recombination in organic solar cells.12-14

If contacts are not selective, $G = R$ does not hold at $V_{oc}$ because charge carriers can be lost due to “surface/interface” recombination when diffusing to the “wrong” electrode. This competing process as well as a superposition of direct and SRH recombination are considered in the numerical simulation, also taking into account the correct charge carrier density profiles and the actual shape of $G$ obtained from optical modeling.28

In Fig. 1(b), the open-circuit voltage is depicted as a function of the illumination intensity for devices comprising ZnPc:C60 blends with three different mixing ratios and the two different HTLs. We first discuss the case of Di-NPD as HTL (open symbols) providing with its lower lying HOMO a sufficiently large built-in potential to avoid recombination at the electrodes. The dashed-dotted lines are a guide to the eye indicating the slopes predicted by Eqs. (2) and (3). Compared to the experimental data, these lines visualize the transition from trap-assisted recombination towards direct recombination with intensity. For intensities larger than 1 sun, mainly direct recombination dominates whereas at intensities lower than a hundredth of a sun, SRH recombination completely governs $V_{oc}$. The transition from SRH to direct recombination with intensity is reasonable as the probability of direct recombination scales with $n^2$ and will superimpose SRH recombination even if all recombination parameters are fixed. In disordered materials, one might find additional reasons for this transition accompanied with the filling of a broad density of states. This results in the picture of free and trapped charges in a shift of the ratio between more mobile (free) and less mobile (trapped) charge carriers towards more free charges with intensity. If the dependence
than Di-NPD. Whereas the interchanged with MeO-TPD, which has a lower IP (5.1 eV)
identical devices except for the hole transport layer being
59 mV/decade, one should consider that this slope implies a
of trap-assisted recombination in a slope between 118 and
work function of MeO-TPD, the built-in field in the device is
reason is that due to the lower IP and subsequently lower
HTL MeO-TPD are reduced for higher light intensities. The
менantly determined values. (b) Open-circuit voltage as a function of illumi-
ment intensity measured with a calibrated reference diode. Roughly,
recombination parameters are supposed to be seen in tran-
lications. Here, SRH recombination and direct recombination are each described by one parameter. They
can be unambiguously determined from $V_{oc}$ as a function of intensity if $E_k^{DA}$ and $N_{C,V}$ are known. For setting $E_k^{DA}$, we choose the ionization potential of ZnPc considering the values measured at the blends with different stoichiometries by photoelectron spectroscopy\(^{32}\) (variations of $\approx \pm 20$ meV allowed). With a constant $E_A(=\text{LUMO})^{32}$ of C$_{60}$ at 4.03 eV (from fit to the $V_{oc}$ data, inverse photoemission spectroscopy gives a variety of data, e.g., 3.94 ± 0.1 eV (Ref. 40)), we fix $E_k^{DA}$ and set $N_{C,V}$ to $10^{17}$ cm$^{-3}$, which is approximately the molecule density. This means we attribute, as already mentioned, the almost constant offset between the curves to a change in $E_k^{DA}$ from 1.06 eV (ZnPc:C$_{60}$ 2:1) to 1.13 eV (1:2) to 1.17 eV (1:3). Alternatively, significant changes of $k_{SRH}$ (factor 10) and $\beta$ (factor 100) with mixing ratio could sufficiently reproduce the data as well. This approach, however, requires a change of both parameters. In the picture of a diffusion-limited recombination for both trap-assisted and direct recombination, a correlation of both rate constants might be reasonable.\(^{22}\) However, changed recombination parameters are supposed to be seen in transient photovoltage measurements.\(^{7}\) As the decay times at a fixed intensity\(^{30}\) are independent of mixing ratio, we con-
clude that the differences in $V_{oc}$ are not attributed to changed recombination but a changed $E_k^{DA}$. Recombination kinetics independent of blend composition were also reported for polymer-based solar cells.\(^{41}\)

The solid lines in Fig. 1(b) indicate that the intensity de-
pendence can be reproduced with fixed values of $k_{SRH} = 10^6 \text{s}^{-1}$ and $\beta = 8 \times 10^{-12} \text{cm}^3\text{s}^{-1}$. Whereas $V_{oc}$ is quite
sensitive to $k_{SRH}$, the value of $\beta$ has to be read as an order of magnitude rather than an exact number. Both values are in the range reported for organic solar cells\(^{12,42}\). The presence of deep electron traps in ZnPc:C$_{60}$ blends was shown by impede-
ance spectroscopy\(^{43}\) with a concentration of $3 \times 10^{16}$ cm$^{-3}$. Assuming a characteristic reported\(^{44}\) capture rate in the order of $10^{10} \text{cm}^3\text{s}^{-1}$ yields the value of $k_{SRH}$ which we find. Langevin theory predicts a slightly (around 2 to 10 times) larger value for $\beta$ than the one assumed here. Furthermore, the fixed $\beta$ indicates that Langevin recombination is probably not applicable in these bulk heterojunction blends because the mobilities vary between different mixing ratios.\(^{29,28}\) Non-applicability of Langevin theory to blends was often observed in literature and pre-factors were introduced.\(^{26}\) Here, for a final statement, further investigations like transient charge extraction measurements are required. However, the changes in $V_{oc}$ with mixing ratio cannot be explained by Langevin recombination. If we had assumed in the simulation that the gap was constant and changes in recombination had to explain the changes of $V_{oc}$ between different mixing ratios, $\beta$ would have to be decreased by two orders of magnitude for the 1:3 compared to the 2:1

![Diagram](https://example.com/diagram.png)

**FIG. 1.** (a) Energies, used in the simulation, for HOMO and LUMO of the ZnPc:C$_{60}$ blends with different mixing ratios and the two different HTL MeO-TPD and Di-NPD. All values are given in eV and are based on experimentally determined values. (b) Open-circuit voltage as a function of illumination intensity measured with a calibrated reference diode. Roughly, $120 \pm 10$ mW cm$^{-2}$ represent 1 sun corrected for spectral mismatch, which slightly depends on the mixing ratio here given in volume percent. The dashed-dotted lines show the slopes expected from Eqs. (2) and (3). Symbols refer to experimental data and lines to simulation data, where a HOMO (≈ HOMO of MeO-TPD) and LUMO (≈ −5.3 eV) represents MeO-TPD and −5.3 eV Di-NPD.

-of $V_{oc}$ on intensity shall be applied to identify the presence of trap-assisted recombination in a slope between 118 and 59 mV/decade, one should consider that this slope implies a region of transition between the two linear regimes (in a $V_{oc} − \ln(\text{intensity})$ plot) instead of fitting with a constant slope as commonly done.\(^{13,14}\)

A variation of the mixing ratio results mainly in an offset of $V_{oc}$. The common shape of the curves in Fig. 1 indicates that the transition from SRH to direct recombination is not affected by the mixing ratio. Therefore, we conclude in a comparison with Eqs. (2) and (3) that either $E_k^{DA}$ or $N_{C,V}$ change with mixing ratio whereas the recombination parameters $\beta$ and $k_{SRH}$ seem to be less influenced by the mixing ratio. Photoelectron spectroscopy measurements, characterizations of the energy of the CT-state,\(^{32}\) and investigations on charge carrier extraction probabilities\(^{39}\) indeed indicate a change of the IP and $E_k^{DA}$ with mixing ratio. The reasons for this effect are most probably changes in the morphology of the blend including the growth modes of ZnPc.\(^{32}\)

The closed symbols in Fig. 1(b) show data for almost identical devices except for the hole transport layer being interchanged with MeO-TPD, which has a lower IP (5.1 eV) than Di-NPD. Whereas the $V_{oc}$ of the ZnPc:C$_{60}$ 2:1 device is not affected, the $V_{oc}$ values of the 1:2 and 1:3 blends with HTL MeO-TPD are reduced for higher light intensities. The reason is that due to the lower IP and subsequently lower work function of MeO-TPD, the built-in field in the device is reduced and an injection barrier from the HTL towards the ZnPc in the blend is formed. This means that for high open-circuit voltages close to the built-in potential, the electrical field as directive driving force vanishes and recombination of electrons at the MeO-TPD/blend interface sets in.\(^{3,31}\) This effect is crucial for the blends with a higher content of C$_{60}$ as the IP of these blends is larger [Fig. 1(a)].

A more quantitative analysis can be done with the aid of numerical simulations. Here, SRH recombination and direct recombination are each described by one parameter. They
were not affected, the carrier extraction probabilities\(^{39}\) indeed indicate a change of the IP and $E_k^{DA}$ with mixing ratio. The reasons for this effect are most probably changes in the morphology of the blend including the growth modes of ZnPc.\(^{32}\)
blend. This change, however, does not follow the trends in mobilities, where the (higher) electron mobility increases roughly by a factor of five and the hole mobility decreases by a comparable extent when increasing the concentration of C60.28

Only setting the IP of the HTL to 5.1 eV and not doing any fitting or changing any other parameter, results in simulation data represented by the dashed lines in Fig. 1(b), which reproduce the experimental data with MeO-TPD as HTL well.

We note that information about geminate recombination cannot be deduced in a study of $V_{oc}$. At $V_{oc}$, a possibly present geminate recombination is in dynamic equilibrium with free charge carriers via dissociation and formation of a bound electron/hole pair. The intensity dependence of $V_{oc}$ will then follow the “recombination” process of free charge carriers into a bound pair (CT exciton). However, we were able to reproduce the complete shape of the $J$-$V$ curve for different generation profiles without considering geminate recombination in competition with field-dependent dissociation of CT-states.28 Therefore, we conclude that geminate recombination does not play a significant role in our material system.

The simulation allows to extract the amount of direct and SRH recombination as a function of light intensity and estimate the losses due to traps. Figure 2(a) shows the relation between radiative and SRH recombination for the 1:3 blend as a function of illumination intensity extracted from the simulation data assuming an IP of the HTL of 5.3 eV (Di-NPD). While the share of direct recombination increases from 5% to 70% with intensity, SRH recombination decreases from 95% to 30%. The differential slope $dV_{oc}/d\log(\text{Intensity})$ also shown in the figure (right axis) can be seen as a measure of the ratio between direct and SRH recombination. At short-circuit (dashed), the ratio between trap-assisted and direct recombination is slightly shifted towards SRH recombination at higher intensities due to lower charge carrier densities at short-circuit conditions compared to open circuit. This trend is inverted for lower light intensities as the charge carrier drift at short-circuit allows charge carriers to move a certain distance increasing the probability of a direct (bimolecular) encounter. Most of the charges are extracted at short circuit. Therefore, the overall recombination at short circuit compared to open circuit is reduced by around 70% to 80% depending on the light intensity. Figure 2(a) shows that even at 1 sun, there is a considerable contribution from SRH recombination ($>50\%$). However, eliminating this process in simulation does not significantly increase $V_{oc}$ (from 0.63 V to 0.64 V). Nevertheless, the efficiency increases from 2.4% to 2.9% due to a higher fill factor without SRH recombination. For intensities lower than 0.1 suns, however, $V_{oc}$ and the efficiency are significantly limited by traps.

Figure 2(b) shows the share of the different recombination mechanisms for the low work function HTL MeO-TPD. In this case, as already discussed, recombination at the electrode can be identified at $V_{oc}$ as a function of light intensity (Fig. 1). Hereby, it is critical to investigate a large intensity range to get unambiguous results. The share of recombination at the electrode (white area) increases with intensity and reaches more than 15%. It correlates well with the reduction of $V_{oc}$ with HTL MeO-TPD compared to Di-NPD, which sets in at an intensity of 1 to 10 mW/cm² in Fig. 1(b). At short circuit (dashed), a significant recombination at the electrode cannot be observed, as charge carriers are driven towards the right electrode due to the electric field caused by the built-in potential.

The discussion so far focused on (separated) charge carriers which resulted from photogeneration. However, a self-consistent simulation is capable of describing the recombination of injected charges as well, as, e.g., demonstrated for bimolecular recombination in Ref. 45. To validate this, the forward current without illumination is investigated. A comparison of experimental with simulated data is shown in Fig. 3. The simulation data are obtained by using the parameters applied for the simulations discussed above and solely deactivating optical generation. Additionally, an experimentally detected shunt is considered, which dominates the $J$-$V$ curves at current densities lower than

![FIG. 2. Simulated share of trap-assisted (SRH) and direct/bimolecular recombination as a function of light intensity and estimate the losses due to traps. Figure 2(a) shows the relation between radiative and SRH recombination for the 1:3 blend as a function of illumination intensity extracted from the simulation data assuming an IP of the HTL of 5.3 eV (Di-NPD). While the share of direct recombination increases from 5% to 70% with intensity, SRH recombination decreases from 95% to 30%. The differential slope $dV_{oc}/d\log(\text{Intensity})$ also shown in the figure (right axis) can be seen as a measure of the ratio between direct and SRH recombination. At short-circuit (dashed), the ratio between trap-assisted and direct recombination is slightly shifted towards SRH recombination at higher intensities due to lower charge carrier densities at short-circuit conditions compared to open circuit. This trend is inverted for lower light intensities as the charge carrier drift at short-circuit allows charge carriers to move a certain distance increasing the probability of a direct (bimolecular) encounter. Most of the charges are extracted at short circuit. Therefore, the overall recombination at short circuit compared to open circuit is reduced by around 70% to 80% depending on the light intensity. Figure 2(a) shows that even at 1 sun, there is a considerable contribution from SRH recombination ($>50\%$). However, eliminating this process in simulation does not significantly increase $V_{oc}$ (from 0.63 V to 0.64 V). Nevertheless, the efficiency increases from 2.4% to 2.9% due to a higher fill factor without SRH recombination. For intensities lower than 0.1 suns, however, $V_{oc}$ and the efficiency are significantly limited by traps.](https://example.com/figure2)

![FIG. 3. Experimental (lines) and simulated (symbols) dark $J$-$V$ curves for different mixing ratios. Solid lines represent devices with HTL Di-NPD and dashed lines devices with HTL MeO-TPD. Open symbols refer to a simulation with a HOMO of the HTL of $-5.3\text{eV}$ and closed symbols to a HOMO of $-5.1\text{eV}$.](https://example.com/figure3)
0.01 mA/cm². Information on recombination is mainly found in the exponential region where the slope is dominated by recombination of injected electrons and holes. This slope corresponds to a diode ideality factor of around 1.9 and is very well reproduced by the simulations. Thus, the initial forward current at voltages up to ≈0.7 V is mainly dominated by SRH recombination, and the parameters obtained from $V_{oc}$ describe also the dark forward current very well. However, these results show that the dominating recombination mechanism under 1 sun does not necessarily prevail in the exponential rise of the forward injection current, i.e., the diode ideality factor. For MeO-TPD, the current onset shifts to lower voltages as the built-in potential is lower in these devices. Especially in the case of the 1:3 blend, an increase of the slope in the exponential regime can be seen, which is reproduced by the simulation as well. This indicates that the recombination at the HTL/blend interface is direct/bimolecular, as assumed in the simulation.

All three recombination processes (direct, SRH, and at the interface to the p-HTL) are predominantly non-radiative and the share of radiative recombination measured by electroluminescence (wavelength $\sim 1100$ nm) is in the order of $10^{-8}$ – $10^{-7}$ and reduced in case of MeO-TPD as HTL where most of the injection current is driven by electrons on C60 recombining at the HTL/blend interface. This observation indicates that the radiative recombination is a bulk recombination process, where electron and hole meet and form an exciton which decays radiatively, although most of the direct electron-hole recombination is non-radiative.

In conclusion, we have identified the dominating recombination process in organic solar cell, using ZnPc:C60 as a model system. Recombination shifts from trap-assisted to direct/bimolecular recombination for higher intensities. This shift is independent of the bulk heterojunction mixing ratio and is seen in a change of the slope of $V_{oc}$ as a function of light intensity. Introducing an injection barrier by changing the hole transport layer decreases $V_{oc}$ for high light intensities due to a lower built-in field, which increases the probability for recombination at the HTL. All three recombination processes are predominantly non-radiative.

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