On the Device Physics of High-Efficiency Ternary Solar Cells

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Mixing a third compound into the active layer of an organic bulk heterojunction solar cell to form a ternary system has become an established way to improve performance. Various models, based on different assumptions regarding the active layer morphology and the energetics, have been proposed but there is neither consensus on the applicability of the various assumptions to different experimental systems, nor on the actual device physics of these, mostly qualitative, models. Kinetic Monte Carlo simulations are used to investigate the role of morphology and relative energy levels of the constituent materials. By comparing with experimental current–voltage characteristics, a consistent picture arises when the (minority) third compound is predominantly incorporated between the other (majority) compounds and has energy levels that are intermediate to those of the binary host. Even if morphologically imperfect, the resulting energy cascade promotes charge separation and reduces recombination, leading to higher fill factors and short-circuit current densities. The open-circuit voltage sits between that of the binary extremes, in agreement with data from an extensive literature review. This leads to selection criteria for third compounds in terms of energetics and miscibility that promote the formation of a cascade morphology in real and energy space.

1. Introduction

Solution-processed conjugated polymers have become a relevant alternative to inorganic semiconductors for applications that require low cost, large area, and flexibility of the devices.[1] Since the first reported bilayer organic photovoltaic (OPV) device,[2] solar cells based on organic semiconducting materials have come a long way of reaching over 18.2% power conversion efficiency (PCE).[3] The original bilayer morphology, comprising an electron-donor material deposited on top of an electron-acceptor material, or vice versa, has a limited interfacial area, resulting in a low photocurrent. The bulk heterojunction, where a partially phase separated blend of donor and acceptor materials is deposited from typically a common solvent, has proven an effective solution to this problem by offering a bicontinuous interpenetrating network for effective exciton dissociation and subsequent extraction of charge carriers.[4–6] However, the active layer thickness of optimized first generation OPV devices was typically limited to about 100 nm due to charge carrier extraction problems, leading to incomplete photon absorption. The latter was further hampered by the limited overlap of the absorption spectra of the constituent materials with the solar spectrum.[7–9] To solve these issues, multijunction or tandem cells were proposed.[6,10–12] Although broadening the absorption window by stacking two subcells on top of each other, this architecture suffers from fabrication complications. To this end, ternary solar cells, which have a single active layer with three constituents, have been proposed and quickly attracted a lot of interest in the research community. With an additional third component or “guest” added to an otherwise optimal binary to form either a two-donor:acceptor (D1:D2:A) or donor:two-acceptor (D:A1:A2) configuration, ternary systems have proven to be an effective strategy of increasing the thickness and thereby enhance the, typically broadened, absorption of the active layers while simultaneously maintaining a simple single-layer fabrication process.[13,14] Despite extensive investigations, the role of the additional donor/acceptor compound in the working mechanism of the ternary system is not quantitatively understood. Broadly classifying, three different models have been proposed, based on the ternary morphology and/or the energetics, being the cascade, alloy, and parallel models.[15–18] As indicated in Figure 1 for a D1:D2:A system, these models are defined by the location and the (relative) energetics of the guest (D2) species, which can be

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either predominantly embedded within the D1 domains, supposedly forming an alloy with energy levels that are intermediate to D1 and D2,\textsuperscript{19} or form separate phase-separated domains in the acceptor phase, leading to parallel D1:A and D2:A junctions, or sit at the interface between donor (D1) and acceptor (A).\textsuperscript{14} In the latter case, an energy cascade is formed when the energy levels of the guest are in between those of the host compounds.\textsuperscript{20,21} Although the proposed models are conceptually appealing and often evoked, a quantitative assessment of their potential merits in terms of device PCE is largely absent.

In this work, we use kinetic Monte Carlo (kMC) simulations to address this issue; specifically, we use our simulations to investigate which of these proposed models can actually provide an improvement over the optimized binary constituents. Ideally, one would use experimentally determined morphologies as independent input for such an endeavor. Impressive progress in the characterization of morphologies in organic semiconductors has been made, and nowadays techniques like solid-state NMR and various X-ray scattering techniques enable identifying crystallographic packing and molecular environments in great detail.\textsuperscript{22–24} Nevertheless, these techniques provide average information about the probed (macroscopic) sample volume and can, so far, not provide information at the mesoscopic level that would be needed to reconstruct the actual arrangement in real and energy space. Likewise, spatially resolved techniques like atomic force microscopy and its derivatives do not (yet) have sufficient resolution, and are limited to the sample surface. As such, we approach the problem from the other end, and start from idealized morphologies as shown in Figure 1. Although physical reality will be more complicated, this has the major advantage that it allows answering the question which concepts are viable and might contribute to improved performance—and which are not. The resulting model is generic in that it can be employed to fully amorphous, partially ordered/aggregated, and polycrystalline systems, provided the dominant transport mechanism is hopping between localized states and appropriate; possibly heterogeneous hopping rates are used. However, kMC models as the one we employ are not predictive when it comes to phase separation, structural, and energetic disorder, or to the transport parameters in general.

Before turning to the detailed workings of the various models for ternary OPV in Figure 1, we will give a compact review of reported ternary devices, as shown in Figure 2, to provide an overview of the phenomena that a formal model should quantify. It should be borne in mind that the universal improvement in PCE upon mixing in a third compound that is suggested by these data is likely the result of a reporting bias, arising because failed systems do not get reported.\textsuperscript{25} Over time, the PCE of reported ternary devices shows a clear upward trend (gray symbols in panel a) that rather seems to reflect a general increase in the overall performance of OPV systems than a specific increase in the ability to make functional ternary systems. In the latter case, one would expect the relative increase in the PCE of the ternary system over the PCE of the corresponding optimal binary (red symbols) to increase with time. This is not observed; if anything, a slightly downward trend is observed. One direct reason for this is the development of nonfullerene acceptors (NFAs), which usually have a stronger and more complementary (w.r.t. the donor)
absorption spectrum than fullerene acceptors, leaving less room for further improvement of the photocurrent by adding a third component. This might be seen as an (inconclusive) indication for the statement by Felekidis et al. that for “absorbers, having a broad and strong absorption spectrum, ternary blends offer no advantage over binary ones”.\footnote{26} Clearly, this point has not been reached in the reported data, justifying further research.

As the PCE is defined as $\text{PCE} = \frac{V_{OC} \times J_{SC} \times FF}{P_i}$, with $P_i$ the incident light power, the relative change in PCE can be decomposed in relative changes in open-circuit voltage $V_{OC}$, short-circuit current density $J_{SC}$, and fill factor (FF) as done on the triple right y-axis of Figure 2b. Although it has sometimes been argued otherwise, the small values of the relative changes in $V_{OC}$ and the absence of a clear correlation with the relative changes in PCE show that changes in $V_{OC}$ are not the driving force for the success of most ternary OPVs.

This limits the practical relevance of the experimental observation that the open-circuit voltage $V_{OC}$ is not simply pinned by the lowest LUMO and highest HOMO in the ternary system, but instead can be continuously tuned between the binary extremes.

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Figure 2. Overview of reported ternary OPV device performances. a) Efficiency of the ternary (grey lines and symbols, left y-axis) and the relative change in the efficiency (red, right y-axis) with respect to optimum binary for various systems. b) The relative change in the efficiency of the ternary (blue lines and symbols, left y-axis) and the contributions from $J_{SC}$ (red), $V_{OC}$ (black), and FF (green). The data sources are ordered with respect to year of publication; a detailed comprehensive list with the system names and references is given in Table S1, Supporting Information.
that is between $V_{OC}^{D1:A}$ and $V_{OC}^{D2:A}$ for a D1:D2:A system.\[26,27\]
Since the first advent of ternary OPV, the physical reason as to why this happens has been debated. Although the cascade, alloy, and parallel models were all argued to be able to describe this finding, both the alloy and the parallel models were shown to have considerable problems in quantifying experimental results. For example, Kouijzer et al. showed that measured external quantum efficiency spectra of ternary PDPP2TBP:PCBM:ICBA solar cells were inconsistent with the notion of alloy formation between both acceptors.\[28\] In general, energy-level hybridization has been observed between carefully matched pairs of organic semiconductors, but it is unlikely that the stringent geometrical and other conditions for this effect to occur are met in generic ternary systems.\[19\] For these reasons, the alloy model will not be further considered here; also, because upon effective hybridization of the D1 and D2 energy levels, both the morphological and energetic aspects of the alloy system become identical to those of a binary system and as such lie outside the scope of this work.

In the same article, Kouijzer et al. have shown that the parallel junction model overestimates the sublinear dependence of $V_{OC}$ on composition.\[28\] A consistent description of this dependence was later given by Felekidis et al. using a simple state-filling model.\[26\]
These state-filling effects are implicitly included in the model that will be presented herein. Some further observations and empirical design rules regarding the tuning of $V_{OC}$ with composition as extracted from the summary of literature data are discussed in Section 1, Supporting Information.

Further inspection of Figure 2b shows that reported improvements in PCE can typically be attributed to either $J_{SC}$ or FF, or both. This points in the direction of a cascade model, cf., Figure 1 (top row), where for a D1:D2:A system, the HOMO and LUMO levels of the guest (D2) sit in between the HOMO and LUMO of the binary host (D1:A) system. Provided the added component also physically sits in between the host donor and acceptor phases, the electron cascading from D1 to D2 to A (and the hole from A to D2 to D1) would both suppress recombination of the geminate electron–hole pair as well as suppress bimolecular recombination. It has been argued that such morphologies self-organize upon favorable (relative) interfacial energetics and solubility of the constituents.\[29–33\]

Irrespective of the precise morphology and energy landscape, the third component can act as a sensitizer to broaden the absorption spectrum and in principle increase $J_{SC}$.\[34,35\] Here, it has to be kept in mind that replacing one absorbing species by another will, at constant active layer thickness, not necessarily lead to an improvement in absorption.\[18\] Likewise, in a simple state-filling picture as in ref. [18], only the ratios of the three components and their relative energy levels matter for $V_{OC}$. However, controlling the morphology is critical in optimizing the performance of any organic solar cell, and in the case of ternary OPV, morphology will determine how much of the potential improvement in $J_{SC}$ and $V_{OC}$ is actually achieved. So far, these morphology–property relations are far from being quantitatively understood. A major problem in this respect is the difficulty, if not impossibility, to experimentally resolve the subtle differences in morphology that would allow deciding which model is most appropriate to interpret the results and, concomitantly, which design rules apply.

Here, we systematically analyze different (simplified) morphologies using kMC simulations of full devices with the goal to investigate their potential relevance for improvements in ternary OPV performance. By considering both the yields of relevant processes like recombination and extraction as well as full current–voltage ($J$–$V$) curves, we find that the parallel junction cannot explain the common experimental observations.

Instead, even morphologically imperfect cascade-type structures can provide significant performance increases, especially in systems where the binary device suffers from recombination losses. To confirm practical relevance, we demonstrate that the developed model can provide a consistent description of experimental $J$–$V$ curves, that is, of the two binaries and the optimized ternary, of representative systems. It is not the goal of this article to claim that specific systems cannot work differently than discussed here. For instance, addition of a small molecular guest might lead to a removal of detrimental traps,\[36\] likewise, the guest might provide a template for improved structural order of (one of) the host constituents, leading to higher mobility and/or less energetic disorder.\[37–39\] While such factors can be included in our model, this is beyond our present purposes and will not be further pursued.

### 2. Numerical Simulations

The conceptual morphologies presented in Figure 1 have been implemented in a kMC model that has been described in detail elsewhere.\[40–42\] The model implements the extended Gaussian disorder model on a cubic lattice.\[43\] The hopping rates are described by the Miller–Abrahams expression and the model includes the dynamics of excitons, interfacial charge transfer (CT) pairs, and free charge carriers. Full Coulomb interactions, including those by image charges in the electrodes and resulting from the periodic boundary conditions in the lateral directions, are considered. The use of a regular lattice and a well-defined unit cell allows to naturally capture the effect of two important critical length scales in any organic solar cell, the typical intersite distance, and the length scale of phase separation. While the distribution of length scales in real samples will lead to a broadening of the associated features and time scales, it is unlikely to lead to conceptual differences. Also in view of the absence of sufficiently detailed experimental data, we refrain from attempts to implement more realistic-looking morphologies, which would come at the cost of additional, unknown parameters.

As the purpose of this section is to investigate the generic properties of the various morphologies, we do not attempt, as in the next section, to describe specific data, and use generic parameters that are representative of OPV systems. Further details of the numerical model and the parameters used for the analysis are given in Section 2, Supporting Information.

The energy levels for the different materials are given in Figure 1. Although state-filling effects are automatically accounted for in the kMC model via an 0.5 eV penalty for double site occupation, they do not necessarily play a major role in the calculated $V_{OC}$ values due to the—also inherently included—slow thermalization of photogenerated charges in the disordered density of states that is characteristic for energetically disordered semiconductors as used in OPV.\[43,44\]
In Figure 3, the simulated $J$–$V$ curves for the ternary morphologies from Figure 1 are plotted with those of the corresponding D1:A and D2:A binaries. For comparison, also the $J$–$V$ curve of a hypothetical, purely random ternary mixture of D1, D2, and A of the same average composition is shown, cf., blue data points. Clearly, the extremely low performance of the latter system confirms that the success of ternary OPV is not due to the mere presence of the third compound. In the absence of a proper spatial arrangement, especially the highest HOMO (of D1) and lowest LUMO (of A) are prone to act as hole and electron traps, leading to very poor long-range charge separation and concomitantly low $J_{SC}$ and FF. A similarly poor performance would result from systems where the second donor is randomly dispersed in the first.

For all three ternary active layers in Figure 3, $V_{OC}$ lies close to the low-$V_{OC}$ binary, in line with typical experimental observations (see Figure S1, Supporting Information). Nevertheless, there are small but significant differences between the three morphologies. While $V_{OC}$ of the random and parallel morphologies are, within numerical accuracy, pinned to $V_{D1:A}$, the cascade system shows a shift toward $V_{D2:A}^{OC}$, in line with the commonly reported experimental observations. The reason for the absence of any $V_{OC}$ improvement for the parallel junction is the fact that at forward bias the low-$V_{OC}$ (D1:A) channel effectively short circuits the high-$V_{OC}$ channel when $V > V_{D1:A}^{OC}$. This finding confirms those in ref. [28]: the parallel junction model is inconsistent with the experimentally observed tunability of the open-circuit voltage. For the random morphology, the lack of $V_{OC}$ improvement cannot be attributed to a short-circuiting effect but rather to the poor charge generation. As shown in Figure S3, Supporting Information, the cascade model does show a continuous tunability of $V_{OC}$ as a function of host ratio.

The cascade ternary morphology also leads to a considerable improvement over the host (D1:A) system in terms of $J_{SC}$. The reason that the D1:A binary shows a lower $J_{SC}$ than the D2:A binary, despite the same exciton generation rates used in the simulations, is the $10\times$ higher hole mobility in the intermediate (guest) compound D2, leading to a reduction in the CT recombination loss, cf., Figure S4, Supporting Information. In the D1: D2:A cascade ternary, holes are still extracted via the D1 phase because of its high(est) HOMO level, but now they are spatially separated from the acceptor phase by the intermediate D2 material. The higher hole mobility in D2 does not play a role in this effect (simulation not shown). Figure S4, Supporting Information, also shows that the CT recombination loss for the cascade ternary remains negligible for all biases, rationalizing the improved FF. Interestingly, at $V_{OC}$ the by far dominant loss channel in this case is diffusion loss, that is, charges recombining at the (nonselective) wrong contact (cf., Figure S4, Supporting Information).

We note that for the system discussed here, none of the ternary systems offers an improvement over the optimal D2:A binary. This is not a flaw of the used model, as will be demonstrated in the comparison with experimental results below, but a consequence of the used parameters. In case, for example, a significantly lower absorption and concomitantly exciton generation rate would have been taken for D2, the ternary cascade would hardly have been affected, whereas $J_{SC}^{D2}$ would have dropped significantly, turning the cascade ternary into the best performing system. The point we want to make here is that when all other factors remain equal, ternaries are unlikely to improve an optimized binary. This point is further highlighted by similar simulations for a slightly smaller and larger intersite distances in Figure S5,S6, Supporting Information. However, as the perfect binary bulk heterojunction system is yet to be reported, ternaries can offer viable ways to overcome some of these imperfections. In the case of the simple example above, the ternary would allow significantly thicker active layers without sacrificing FF due to recombination, and thereby offer improved absorption, even if the guest compound is hardly absorbing.\[45-47\] This scenario might be particularly relevant for D:A1:A2 systems where the guest compound is a weakly absorbing fullerene, as is also the case in the PM6:Y6:PC71BM system below.

In real systems, the self-organization of a three-component mixture in a cascade morphology is driven by (differences in) miscibility and interface energetics, which is a stochastic process that is unlikely to result in a perfectly closed guest layer sitting between the host materials. To study the impact of the resulting “leakiness” on performance, we discern different grades of two types of leaks: 1) exchange or 2) replacement of a guest site with a host donor or acceptor site. The detailed results can be found in Section 3, Figure S7 and S8, Supporting Information, and show that even at very high levels of leakiness, a cascade-type morphology offers some advantage over the binary host system: a morphologically perfect cascade, which is unlikely to form by self-organization of real systems, is not needed. As before, this advantage increases when the host suffers from larger (CT) recombination losses, which is in line with the above-noticed decreasing benefit of ternary OPV when the binary subsystems become more optimal.
3. Experimental Results and Simulations

To test the practical relevance of our model in general and the above conclusions in particular, we studied the J–V curves of several well-performing ternary systems. Note that these are all D:A1:A2 systems, where in the PM6:Y6:PC71BM and PBDB-T:Y1:PC71BM systems the PC71BM (guest) LUMO lies in between the LUMO levels in the host; in the PCE10:PC71BM:ICBA system, the ICBA is intermediate. Details on the sample fabrication and measurements can be found in the Experimental Section; performance characteristics are provided in Table S3, Supporting Information. The measured J–V curves of the binary systems and the optimized ternary are plotted in Figure 4, along with the results from kMC simulations. The parameters used for the latter are given in Table S4, Supporting Information, in Section 4, Supporting Information. For all systems, the optimal ternary was found for low guest concentrations, and improvements in terms of V_{oc} were minimal; instead J_{sc} and/or FF were found to increase. These findings are fully consistent with the discussions above.

The simplified nature of especially the morphology used in the model and the constraints put on the model parameters, see discussion in Section 4, Supporting Information, make it unrealistic to expect a perfect fit for all devices. Nevertheless, under the assumption of a cascaded morphology, a satisfactory agreement is reached and the experimentally observed trends in all systems are well reproduced. In other words, the cascade morphology allows for a (almost) quantitative description of typical J–V curves of optimized ternary OPV devices using realistic input parameters.

The consistent description of the experimental trends is the main result of Figure 4. Nevertheless, some specific points are worth mentioning. PM6:Y6 (Figure 4a) is a highly studied nonfullerene system that in its binary form can reach efficiencies up to 16.88%.[48] In our hands, the binary reaches 13% PCE, which can be improved to 14% by addition of PC_{71}BM. As explained above, it is not evident that addition of a poor absorber leads to an increased device performance. Likewise, the small fullerene fraction (A1:A2 = 1:2:0.2) basically precludes the formation of percolating fullerene phases as would be needed to make a parallel junction device. Hence, suppression of recombination losses in a cascade-type morphology is one, if not the only, natural explanation for the observed performance increase. A similar conclusion can be drawn for the PBDB-T:Y1:PC_{71}BM system in Figure 4b. The PCE10:PC_{71}BM:ICBA system is somewhat different as none of the used acceptors contributes significantly to absorption. Also in this case, the ICBA guest can be advantageously incorporated in the PCE10:PC_{71}BM blend, despite the fact that the optimal PCE10:ICBA binary shows a significantly lower short-circuit current. As explained above, the role of the ICBA then becomes that of a spacer between the dominant hole and electron transport channels, suppressing recombination.

Combined, the data in Figure 4 are fully consistent with the general discussion of the cascade-type ternary systems in the context of Figure 3. Note, specifically, that both in the experiments and in the model calculations, the optimized ternary outperforms the binary parent systems, in line with typical systems reported in the literature. The contrast with the data in Figure 3, where the D2:A binary system outperforms the ternary system, shows that even when a perfect cascade is formed, the ternary system is not guaranteed to be better than both constituent binaries.

Although the experiments shown here are for D:A1:A2 systems, the conclusions presented herein are relevant for D1:D2:A systems as well—as noted above, the data in Figure 3 are consistent with those in Figure 3 which are for D1:D2:A systems. As explained in the caption of Figure 1, for any two-acceptor system an equivalent two-donor system can be drawn. Likewise, the literature survey presented in Figure 2 does not suggest any fundamental differences between reported two-donor and two-acceptor systems, that is, differences that would require a fundamentally different modeling ansatz. Of course, when translating the results from one system to the other, one must account for differences in absorption—the absorption coefficients of fullerene acceptors are typically much less than those of nonfullerenes (and donors), hopping parameters, miscibility, etc. It is in that context important that the data in Figure 4 show that our model provides a consistent description of systems where only one and two components absorb (see also last row in

Figure 4. Experimental J–V curves (solid lines) and kMC model calculations (open symbols and dotted lines) for a) PM6:Y6:PC_{71}BM, b) PBDB-T:Y1:PC_{71}BM, and c) PCE10:PC_{71}BM:ICBA ternary and binary systems.
Table S4, Supporting Information); the case where also the third (guest) component absorbs, as in Figure 3, was not experimentally investigated but is not expected to behave fundamentally different.

4. Conclusion

Summarizing, we have shown that reported literature data for ternary OPV systems indicate that performance improvements of optimized ternaries with respect to the corresponding binary devices are typically due to improvements in $J_{SC}$ and FF and not in VOC. Systematic kMC modeling shows that these findings can be consistently explained when one assumes that the guest component sits between the donor- and acceptor-rich phases of the host system, both in real space and in energy space. The resulting energy cascade does not have to be perfect to offer benefit to the system. However, ternary OPV systems indicate that performance improvements by ternary are unlikely to get reported. Although our modeling does not at all rule out alternative scenarios for improvement-by-ternary, one may speculate that some fraction of failed ternaries is made up by those material combinations that fail to show the right self-organization. Thereby, the current work strongly suggests that candidate materials for ternary OPV should not only be selected on basis of suitable (cascade-type) morphology, even if the cascade is leaky or only present for one carrier type. Nevertheless, ternaries are no panacea, and one has to bear in mind that failed attempts to improve systems by going ternary are unlikely to get reported. Although our modeling does not at all rule out alternative scenarios for improvement-by-ternary, one may speculate that some fraction of failed ternaries is made up by those material combinations that fail to show the right self-organization. Thereby, the current work strongly suggests that candidate materials for ternary OPV should not only be selected on basis of suitable (cascade-friendly) energy levels but also on the basis of miscibility and surface energies that should promote the desired spatial self-organization.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

kinetic Monte Carlo, modeling, organic solar cells, ternary systems

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