

Dark Side of Organic Solar Cells: How Triplet Excitons Shape Charge Recombination and Efficiency Limits

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The power-conversion efficiency of organic solar cells has recently surpassed 20%, yet a unified framework that captures the underlying photophysical mechanisms remains elusive. These devices operate via a complex interplay between multiple excited states—excitons, charge transfer (CT), and charge-separated states—arising at the donor-acceptor heterojunction. Here, we present a comprehensive 5-state kinetic model that, for the first time, integrates both singlet and triplet CT states and explicitly incorporates the formation and resplitting of local triplet excitons, fully parametrized by the interfacial energy offset. This model not only reproduces essential photovoltaic observables—such as charge generation efficiency, photoluminescence, electroluminescence, and the Langevin reduction factor—but also reveals that triplet-mediated recombination governs device performance across a wide range of energy offsets. Strikingly, we find that in systems with moderate offset, triplet decay emerges as the dominant recombination pathway, reconciling long-standing experimental findings, including those in benchmark systems such as PM6:Y6. The model offers a mechanistic explanation for the empirically observed link between energy offset and non-Langevin recombination, and accurately predicts the device efficiency across different material systems. Notably, it identifies a singlet-CT offset of ~ 150 meV as optimal for efficient charge separation while suppressing loss pathways. These results advance the fundamental understanding of exciton and charge dynamics in organic photovoltaics, and provide predictive guidance for overcoming the apparent efficiency ceiling of $\sim 20\%$ for binary donor-acceptor blends, paving the way for next-generation high-performance devices.

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I. INTRODUCTION

The rapid progress of organic solar cells (OSCs) in recent years, following the advent of non-fullerene acceptors (NFAs), has brought them to the forefront of photovoltaic research with the power-conversion efficiency (PCE) having surpassed the 20% benchmark. Yet, significant voltage and fill factor (FF) loss in OSCs compared to inorganic devices remains a major challenge, even in high-performing systems.

It is widely accepted that free charge generation in NFA-based OSCs, following light absorption into bound singlet

excitons (LE), is mediated by interfacial charge transfer (CT) states, constituting an electron-hole pair extending over the donor:acceptor interface that is formed after hole transfer from the acceptor (A) to the donor (D) [1]. The formation of these intermediary CT states relies heavily on the energetic driving force between LE and CT, often estimated as the highest occupied molecular orbital (HOMO) energy offset between donor and acceptor (Δ_{HOMO}). At the same time, this driving force introduces a significant energy loss, seen as the reduction of the open-circuit voltage (V_{oc}) to values usually below 1 V, much lower than the optical band gaps of the organic materials would imply. Reducing said offset to minimize the voltage loss in turn comes at the expense of the free charge generation and leads to a reduction of the short-circuit current density (J_{sc}) and worsening of the FF [2].

Recently, studies have shown material combinations with minimal driving force that still achieve high performance [3–5]—suggesting that current generation remains uncompromised. Reported energy levels, however, show

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a large variation based, in part, on the different measurement methods, fabrication techniques, and materials used [6]. We recently highlighted the critical role of LE dissociation (probed by photoluminescence) in charge generation using a 2-state model, wherein even at high CT dissociation efficiencies, a Δ_{HOMO} of at least 0.3 eV is needed to give rise to efficient free charge generation that is not primarily compromised by LE decay [7]. Previous estimates of the minimum offset were set at roughly 0.5 eV [8]. Convincing fits to both the internal quantum efficiency (IQE) as well as the non-radiative voltage loss (via electroluminescence) were presented by Classen *et al.*, emphasizing the importance of long exciton lifetimes to counteract the slow exciton dissociation resulting from small driving forces [9]. Price *et al.* have shown the effectiveness of such kinetic models at recreating time-resolved measurements, such as transient absorption spectroscopy (TAS) [10]. Sandberg *et al.* expanded this framework to predict PCE limits and uncover kinetic requirements to reach these [11]. However, a holistic understanding of OSC device performance remains incomplete without consideration of triplet states and especially their recombination [12,13], which are believed to impact charge recombination detrimentally—affecting the non-radiative voltage loss and the fill factor.

In this work, we aim to develop a comprehensive model capable of simultaneously reproducing multiple key metrics, including the internal generation efficiency (IGE), photoluminescence and electroluminescence quantum yield (PLQY and ELQY), and the Langevin reduction factor (γ). As such, we show how the simple 2-state model, based solely on LE and CT states, inadequately describes the entire solar-cell physics. We resolve these shortcomings by introducing localized triplet states—which are undoubtedly present in organic material systems [14–18]—unifying the mechanisms of free charge generation and recombination. Our analysis uncovers the fundamental role of triplet-mediated recombination in defining performance limits of high-efficiency systems and lays the theoretical groundwork essential for overcoming the current $\sim 20\%$ efficiency plateau in OSCs based on D:A binary blends.

II. THEORY AND MODEL

A. Modeling organic solar-cell kinetics

In typical solar-cell operation, excitons are photogenerated through light absorption (G_{LE}) and are assumed to occupy a defined energy level: the local singlet exciton energy, LE, of the acceptor. These either decay to the ground state S_0 (with a rate coefficient of $k_{f,\text{LE}}$) or dissociate ($k_{d,\text{LE}}$) into singlet CT states (CT1). These can either back-transfer to the LE ($k_{r,\text{LE}}$), decay to S_0 ($k_{f,\text{CT}}$), or, ideally dissociate further ($k_{d,\text{CT}}$) into free charges (CS).

Direct generation of CS is also possible through electroinjection (G_{CS}), after which they non-geminately recombine ($k_{r,\text{CT}}$) to populate either the triplet CT state (CT3) or the CT1 in a 3:1 ratio, according to quantum mechanics. The CT3 can again dissociate ($k_{d,\text{CT3}}$) into CS or form ($k_{r,\text{T}}$) localized triplet excitons (T). Lastly, these triplets either decay to S_0 ($k_{f,\text{T}}$) or redissociate ($k_{d,\text{T}}$) to CT3.

Importantly, the direct decay of CS or CT3 to the ground state is neglected. The exchange between the different CT or exciton populations via intersystem crossing (ISC) is also ignored, as it is too slow to compete with the other pathways; k_{ISC} has been shown to be orders of magnitude below singlet (LE and CT1) decay and dissociation rate coefficients [13,14]. Extraction of free charges is likewise not considered explicitly, as described below. The two CT dissociation coefficients ($k_{d,\text{CT}}$ and $k_{d,\text{CT3}}$) are assumed to be equal due to their degeneracy, $E_{\text{CT1}} \cong E_{\text{CT3}}$, but remain distinguishable in the equations.

The model described here is visualized in Fig. 1 and gives rise to the following system of rate equations:

$$\frac{dn_{\text{LE}}}{dt} = G_{\text{LE}} - n_{\text{LE}}(k_{d,\text{LE}} + k_{f,\text{LE}}) + n_{\text{CT1}}k_{r,\text{LE}}, \quad (1a)$$

$$\begin{aligned} \frac{dn_{\text{CT1}}}{dt} = & n_{\text{LE}}k_{d,\text{LE}} - n_{\text{CT1}}(k_{r,\text{LE}} + k_{d,\text{CT}} + k_{f,\text{CT}}) \\ & + n_{\text{CS}}^2k_{r,\text{CT}}, \end{aligned} \quad (1b)$$

$$\frac{dn_{\text{CS}}}{dt} = G_{\text{CS}} + n_{\text{CT1}}k_{d,\text{CT}} - n_{\text{CS}}^24k_{r,\text{CT}} + n_{\text{CT3}}k_{d,\text{CT3}}, \quad (1c)$$

$$\frac{dn_{\text{CT3}}}{dt} = n_{\text{CS}}^23k_{r,\text{CT}} - n_{\text{CT3}}(k_{d,\text{CT3}} + k_{r,\text{T}}) + n_{\text{T}}k_{d,\text{T}}, \quad (1d)$$

$$\frac{dn_{\text{T}}}{dt} = n_{\text{CT3}}k_{r,\text{T}} - n_{\text{T}}(k_{d,\text{T}} + k_{f,\text{T}}). \quad (1e)$$

In steady-state conditions, where $dn_x/dt = 0$, this system of equations is solved for the population densities n_x , as detailed in Note S2.5 in the Supplemental Material [19].

B. Device metrics

1. Internal generation efficiency

The efficiencies associated with the LE and CT dissociation processes ($\eta_{d,\text{LE}}$ and $\eta_{d,\text{CT}}$) are given by considering the competition between the different processes from each state:

$$\eta_{d,\text{LE}} = \frac{k_{d,\text{LE}}}{k_{d,\text{LE}} + k_{f,\text{LE}}}, \quad (2a)$$

$$\eta_{d,\text{CT}} = \frac{k_{d,\text{CT}}}{k_{r,\text{LE}}^{\text{eff}} + k_{d,\text{CT}} + k_{f,\text{CT}}}, \quad (2b)$$

where $k_{r,\text{LE}}^{\text{eff}} = [1 - \eta_{d,\text{LE}}]k_{r,\text{LE}}$ is the effective back-transfer rate coefficient to LE, reduced by the LE dissociation efficiency (cf. Ref. [11]).

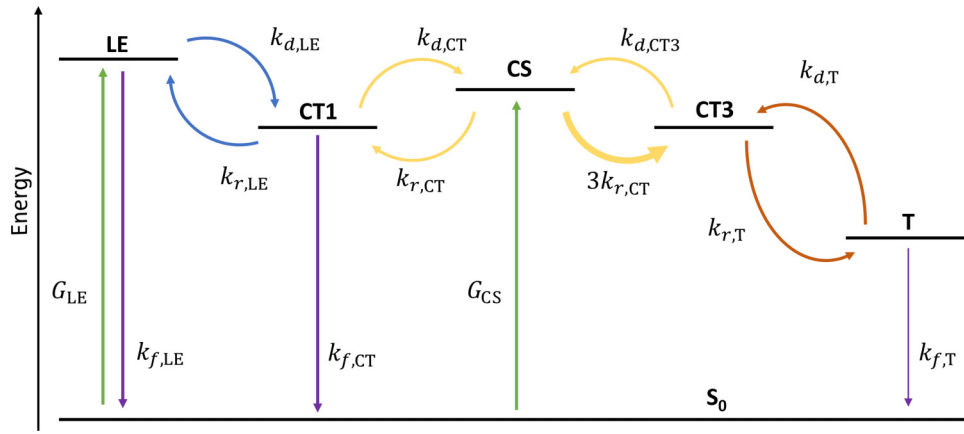


FIG. 1. A schematic energy-level diagram including relevant kinetics for a 5-state model of organic solar cells. It is made up of local singlet and triplet excitons (LE and T), the singlet and triplet charge transfer states (CT1 and CT3), as well as the separated charges (CS). The generation rates into LE and CS (G_{LE} and G_{CS}) serve as input, while decay from LE, CT1, and T ($k_{f,LE}$, $k_{f,CT}$, and $k_{f,T}$) serves as the loss channels. Competing processes on CT1 include dissociation and reformation of the LE ($k_{d,LE}$ and $k_{r,LE}$) and of the CS ($k_{d,CT}$ and $k_{r,CT}$). Analogously, the triplet side includes dissociation and formation of the T ($k_{d,T}$ and $k_{r,T}$) and of the CT3 ($k_{d,CT3}$ and $3k_{r,CT}$, with a triplet degeneracy factor of 3).

The free charge (photo)generation efficiency is the product of these two dissociation efficiencies (more in Note S2.2 in the Supplemental Material [19]; cf. Ref. [7]):

$$\eta_{CG} = \eta_{d,LE} \eta_{d,CT} = \frac{k_{d,LE} k_{d,CT}}{(k_{d,LE} + k_{f,LE})(k_{d,CT} + k_{f,CT}) + k_{r,LE} k_{f,LE}}, \quad (3)$$

and is used to fit the IGE—the ratio of the number of generated free charges to the number of absorbed photons—as one of the key metrics determining the efficiency of a solar cell. Note that the IGE is different from the internal quantum efficiency which also accounts for charge extraction, which we do not consider here.

2. Photo- and electroluminescence quantum yield

We define the *PL decay efficiency* at V_{oc} as the efficiency of LE decay when utilizing only photoexcitation:

$$\eta_{PL} = \frac{n_{LE}(G_{CS} = 0)k_{f,LE}}{G_{LE}}. \quad (4)$$

Mirroring this, the *EL decay efficiency* is defined as the efficiency of LE decay when utilizing only electroinjection:

$$\eta_{EL} = \frac{n_{LE}(G_{LE} = 0)k_{f,LE}}{G_{CS}}. \quad (5)$$

These decay efficiencies represent the fraction of total excitations (either G_{LE} or G_{CS}) that decay through the LE state. We will use these efficiencies to fit the experimental PLQY and ELQY data, which provide valuable insight into

charge recombination and voltage loss mechanisms [20]. However, the decay efficiency cannot be measured directly because only a fraction of the total decay is *radiative* and measurable as luminescence, while the remainder decays to the ground state *non-radiatively* [21].

In order to compare the experimental data to the calculated result from Eq. (4), the measured PLQY of the blend is normalized by that of the acceptor. Following absorption and Förster resonance energy transfer (FRET), we assume that all excitons reside on the lower-band-gap material, even when blended with another material [8,11]. Consequently, recombination proceeds via the acceptor LE rather than the donor, and the radiative fraction of exciton decay in donor-acceptor blends (D:A) is identical to that of the neat acceptor. We have validated this in a previous work by modeling the blend PLQY using the neat PLQY for various material combinations (in the absence of LE-CT hybridization) [7].

Optical outcoupling issues that additionally reduce the measured luminescence signal—such as reabsorption in the device, cavity effects arising from reflective interfaces, 2π radiation, etc.—are also corrected for using the same approach. Experimentally, the neat acceptor is dispersed in a polystyrene matrix (PS:A) with comparable thickness, to more closely resemble the morphology and aggregation of the acceptor in the D:A blend. Thus, the experimental PL decay efficiency is calculated as (see Note S2.2 in the Supplemental Material [19]):

$$PLE = PLQY_{D:A} / PLQY_{PS:A}. \quad (6)$$

Given identical sample architecture and measurement configuration, which ensures the same radiative fraction and

outcoupling efficiency, the experimental EL decay efficiency is similarly calculated as

$$\text{ELE} = \text{ELQY}_{\text{D:A}}/\text{PLQY}_{\text{PS:A}}. \quad (7)$$

We acknowledge here that hybridization of the LE with the CT1 may occur in low-offset systems [22,23]. This will potentially increase the radiative decay rate of CT1, meaning that the blend emission is no longer determined solely by the radiative decay of LE. However, detailed 3-level calculations as well as experiments have shown that the contribution of the CT emission to the total emission remains small, even in cases of small energy offset [24]. We also see no evidence of heightened CT emission in our experimental data, as visualized in Fig. S4 in the Supplemental Material [19]. The other extreme to consider is a large LE-CT offset, where fast LE dissociation and slow LE reformation make the CT1 decay a prominent, if not dominant, radiative decay channel [23]. Our model assumptions are no longer valid for such high-offset systems but such systems are not in our interest, as they generally exhibit very large voltage losses.

3. Langevin reduction factor

Recombination in disordered low-mobility systems—such as in OSCs—is typically described as free charge encounters leading to CT states, as explained by Langevin theory [25]. The *Langevin recombination coefficient* in our model is thereby given as

$$k_L = 4k_{r,\text{CT}}, \quad (8)$$

where the factor of 4 accounts for encounters to both singlet and triplet CT states. In the steady-state condition, the state densities reach equilibrium, whereby the generation into CS, either by CT splitting upon photogeneration at V_{oc} or electroinjection, is balanced by the bimolecular recombination from CS, with the rate R_2 and coefficient k_2 . We assume in the following that k_2 is the same for photogenerated and electroinjected charges. Therefore, to calculate k_2 , we set $G_{\text{LE}} = 0$, so that

$$R_2 = k_2 n_{\text{CS}}^2 = G_{\text{CS}} \quad (9)$$

(for a more extensive look, see Eq. (S5.8) in the Supplemental Material [19]). The Langevin reduction factor, an important metric to describe the underlying recombination mechanisms, is then defined as the ratio

$$\gamma = \frac{k_2}{k_L}, \quad (10)$$

which describes the suppression of charge recombination (k_2) relative to the Langevin limit (k_L). Increased charge generation efficiency (due to CT dissociation) as well as

suppressed triplet exciton formation was previously shown as a means to reduce bimolecular recombination [26,27]. Equation (15) shows how the reduction factor can be written in terms of the (singlet and triplet) CT redissociation, after their formation from CS encounters.

C. Transfer rates according to Marcus theory

The famous Marcus equation for transfer rate coefficients, as given in Ref. [28], reads

$$k(\Delta E) = \frac{H_{ab}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left\{ -\frac{(\lambda + \Delta E)^2}{4\lambda k_B T} \right\}, \quad (11)$$

with a driving force ΔE (as the Gibbs free energy difference between the initial and final state), temperature T , Boltzmann constant k_B , and reduced Planck constant $\hbar$. The electronic coupling strength H_{ab} and reorganization energy λ have been obtained from density functional theory (DFT) calculations in Ref. [7]. The total value of λ consists of the inner and outer reorganization energy, where values of around 200 meV have been reported for the latter [29]. Note that the same H_{ab} and λ values are used for the processes between LE and CT1 as well as between CT3 and T, a simplification that we justify with Figs. S7(a) and S7(b) in the Supplemental Material [19].

We model the exciton dissociation and (re)formation rate coefficients in the Marcus frame, as commonly employed [30,31]:

$$k_{d,\text{LE}} = 0.1k(-\Delta E_{\text{LE-CT}}), \quad (12a)$$

$$k_{r,\text{LE}} = k(\Delta E_{\text{LE-CT}}), \quad (12b)$$

$$k_{d,\text{T}} = k(-\Delta E_{\text{T-CT}}), \quad (12c)$$

$$k_{r,\text{T}} = k(\Delta E_{\text{T-CT}}), \quad (12d)$$

where the driving force for the LE to dissociate into CT states is provided by their energy difference and exciton splitting readily occurs for a positive offset, i.e., $\Delta E_{\text{LE-CT}} = E_{\text{LE}} - E_{\text{CT}} > 0$. For triplet excitons, we similarly define the driving force as $\Delta E_{\text{T-CT}} = \Delta E_{\text{LE-CT}} - \Delta E_{\text{ST}}$, with the singlet-triplet energy difference $\Delta E_{\text{ST}} = E_{\text{LE}} - E_{\text{T}}$. In organic phase-separated bulk heterojunctions (BHJs), where most photoexcited NFA molecules lack a neighboring donor molecule to undergo hole transfer, the limited diffusion of the exciton to the interface is considered via a 0.1 prefactor in the singlet exciton dissociation rate coefficient [32]. This can also be interpreted as a mismatch between the densities of states at the interface (the CT) and in the bulk (the LE): with $g(\text{LE})/g(\text{CT}) = 10$, as in Ref. [9]. The triplet excitons, which only form at the interfaces from CT3 recombination, such that $g(\text{T}) = g(\text{CT3})$, lack this prefactor.

The aforementioned parameter values used in the model are condensed in Table I. Efficient CT dissociation

TABLE I. The parameters used for the steady-state model. Most values are fixed to typical representative values. Some values are slightly variable (denoted by $\approx$) and will act as our fitting variables, within reasonable ranges. The driving force $\Delta E_{\text{CT-LE}}$ acts as the x axis. There are seven primary parameters defining the model, indicated in bold type. The CT1 reformation is treated as a free parameter in the model and can be set arbitrarily due to its balance with CT dissociation.

Symbol	Description	Value	References
$G_{\text{LE}}, G_{\text{CS}}$	Photogeneration and electroinjection rates	$1 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$	
$k_{f,\text{LE}}$	Singlet exciton decay	$1 \times 10^9 \text{ s}^{-1}$	[1,9,33–35]
$k_{f,\text{CT}}$	CT1 decay	$1 \times 10^9 \text{ s}^{-1}$	[26,30,36]
$k_{f,\text{T}}$	Triplet decay	$\approx 1 - 10 \times 10^6 \text{ s}^{-1}$	[16]
$k_{d,\text{CT}}, k_{d,\text{CT3}}$	CT dissociation	$1 \times 10^{11} \text{ s}^{-1}$	[14]
$k_{r,\text{CT}}$	CT1 reformation	$2.5 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$	[19]
$k_{d,\text{LE}}, k_{d,\text{T}}, k_{r,\text{LE}}, k_{r,\text{T}}$	Exciton dissociation and reformation	Marcus rates	[31], Eq. (11)
H_{ab}	Coupling strength	0.01 eV	[7,13,37]
λ	Reorganization energy	$\approx 0.5 \text{ eV}$	[7,31]
ΔE_{ST}	Singlet-triplet offset	$\approx 0.3 \text{ eV}$	[38]
$\Delta E_{\text{LE-CT}}$	Driving force	$-0.4 \text{ eV to } 0.4 \text{ eV}$	

throughout is maintained by an offset-independent CT dissociation rate coefficient, supported by the findings in Fig. S6(e) in the Supplemental Material [19], wherein inefficient CT dissociation fails to describe the experimental data. Figure S5 in the Supplemental Material [19] gives a more nuanced look on inefficient CT dissociation at low-offset.

Here, the reported numbers for Y6 and its binary blend with PM6 serve as guidance. Nevertheless, even for these well-studied materials, some values vary significantly. For example, while values for the LE-CT1 electron coupling in PM6:Y6 from DFT calculations are rather consistent (around 10 meV), the prediction of the inner reorganization energy ranges quite significantly, between 100 and 325 meV [7,13,37]. Also, while most studies report a LE decay time for neat Y6 of around 0.8–1.5 ns [9,33–35], shorter PL decay times were occasionally reported; such as 250 ps [39]. The situation is even more complex for CT1 decay times, which depend, among other factors, on the CT energy following the energy-gap law [40,41]. However, a decay time of ~ 1 ns seems to be reasonable value for D:A blends with sufficiently large V_{oc} (and therefore CT energy) [26,36,41].

Studies reporting the reorganization energy of the triplet (T-CT3) process are quite scarce and inconsistent. It is reported to be similar to that of the singlet (LE-CT1) process [13], much higher for recombination to triplet excitons than for singlet exciton dissociation [42] or much lower—around 100 meV [30]. We already note here that our model likewise does not yield a definitive conclusion (see Sec. IV B). Triplet lifetimes are reported to be on the order of tens of microseconds [16], but can be reduced to only a few microseconds or less by triplet-polaron annihilation [14]. Lastly, the LE energy in NFAs has been shown to be greatly reduced by their fluorinated end-group $\pi - \pi$ stacking, resulting in ΔE_{ST} as low as 0.3 eV; demonstrated for Y6 [38].

III. ANALYSIS: MODEL COMPARISONS

The exact solutions to all models introduced here can be found in Notes S2.1–S2.5 in the Supplemental Material [19].

A. The singlet branch (the 2-state model)

Since, in the absence of intersystem crossing, the free charge photogeneration efficiency η_{CG} is solely determined by the LE and CT1 dissociation efficiencies (see Eq. (3)), it is unaffected by the presence or kinetics of the CT3 or T states, and should therefore remain unchanged when these states are introduced. The PL efficiency η_{PL} , largely playing in the singlet branch as well, should similarly remain independent. Figure 2(a) visualizes the changes between the simplest 2-state model, encompassing only the LE and CT1 states, and the complete 5-state model as described above. Note that we plot $\Delta E_{\text{LE-CT}}$ here, mirrored to $\Delta E_{\text{CT-LE}}$ in our recent work [7].

In both models, these two metrics— η_{CG} and η_{PL} —can be very accurately fitted using the same set of parameters, with $\lambda \approx 550$ meV—the reorganization energy for the exciton-to-CT charge transfer processes. The IGE and PL trends in Fig. 2(a) are straightforward. A negative driving force (LE below CT1) inhibits LE dissociation, whereby almost all excitons remain in the LE state and decay from there. Conversely, a positive driving force (LE above CT1) promotes LE dissociation, depleting the LE state in favor of CT1 and thus reducing the LE decay. With efficient CT dissociation, the CT1 population is directly linked to free charge generation (see Eq. (S2.1) in the Supplemental Material [19]). In the “transition region” between these two regimes, the LE reformation and dissociation compete, with the balance being determined by the offset (Eq. (26)), resulting in the characteristic sigmoidal shape observed experimentally.

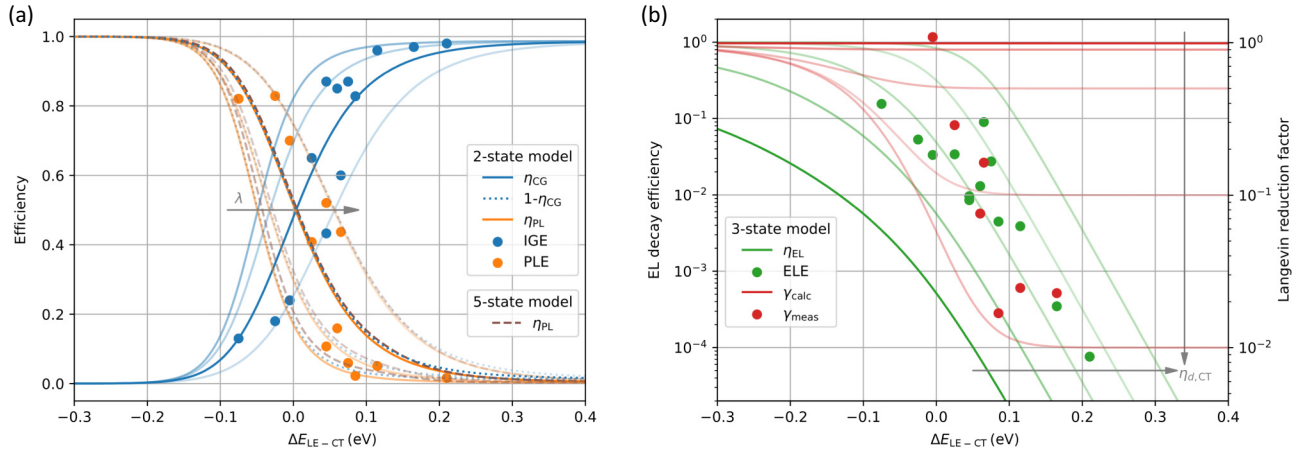


FIG. 2. Two states capture the IGE and PLQY accurately. Three states describe but overestimate ELE. (a) Free charge generation and PL decay efficiency, η_{CG} and η_{PL} , in the 2-state model, shown for different singlet reorganization energies $\lambda_{LE}/\text{eV} = 0.35, 0.45, 0.55$, and 0.65 as indicated by the arrow. It can be seen how the singlet decay competes with free charge generation with $\eta_{PL} = 1 - \eta_{CG}$, provided that CT dissociation is fast (cf. Ref. [7]). The PL decay efficiency in the 5-state model is shown for comparison (dashed brown line). (b) The EL decay efficiency and Langevin reduction factor, η_{EL} and γ_{calc} , in the 3-state model where free charges encounter to (re)form CT1 states, shown for increasing CT1 dissociation efficiencies, $\eta_{d,CT} = 0.01, 0.1, 0.5, 0.95$, and 0.99 , following the directions of the arrows. The experimental data are overlaid as circles.

Figure 2(a) also demonstrates how the charge generation is in direct competition with the LE decay, in agreement with Ref. [7], maintaining the relationship $\eta_{CG} + \eta_{PL} = 1$ throughout. Only in the case of very efficient LE dissociation, where high-CT populations (cf. Fig. 5) lead to high CT decay losses, does a slight deviation appear and result in $\eta_{CG} + \eta_{PL} < 1$. Interestingly, the transition region in the 5-state model shows $\eta_{CG} + \eta_{PL} > 1$. While the sum of these efficiencies exceeding unity might initially appear unphysical, it simply arises from free charge recombination back to CT1 (and subsequently LE), which was not considered in the 2-state model, thereby counting toward both η_{CG} and η_{PL} . This behavior is restricted to the transition region, where neither the LE reformation nor the LE dissociation dominates, so that $k_{r,LE}^{\text{eff}}$ is non-zero. Note that some transient experiments such as time-delayed collection field (TDCF) or transient absorption spectroscopy allow probing of the initial state of free charge generation without contributions from CS recombination. Consequently, the results from these measurements can be described by the 2-state model.

B. Free charge recombination (the 3-state model)

We now turn to the prediction of the electroluminescence efficiency and the Langevin reduction factor, by including the generation and recombination of the CS state, with the generation rate G_{CS} . Since we do not consider trap-assisted recombination, free charge recombination must proceed through the reformation to and the subsequent decay of the CT state (and to a lesser extent the LE state). We mention already here that neither η_{EL} nor

γ depends on the value of the bimolecular encounter rate coefficient of free charges to CT1 due to the balance of CS encounters with CT dissociation (cf. Ref. [11]). A smaller (higher) $k_{r,CT}$ will only increase (decrease) n_{CS} , without affecting the CT or LE populations.

Figure 2(b) visualizes both η_{EL} and γ for different values of the CT1 dissociation efficiency $\eta_{d,CT}$. The 3-state model captures the overall dependence of ELE and γ on ΔE_{LE-CT} , both decreasing with offset, but fails to predict their absolute values. The lightest line corresponds to the values given in Table I, with $\eta_{d,CT} = 0.99$ through $k_{d,CT} = 10^{11} \text{ s}^{-1}$ and $k_{f,CT} = 10^9 \text{ s}^{-1}$. For this set of parameters, the ELE is overestimated by more than an order of magnitude and the reduction of γ happens roughly 0.1 eV earlier than anticipated. The ELE values can be reconciled by assuming a dissociation efficiency less than unity, i.e., $\eta_{d,CT} \approx 0.5$. However, this is in contrast with the charge generation pathway, where efficient CT1 dissociation is necessary to reach an IGE close to unity as in the 2-state model (Fig. S2(a) in the Supplemental Material [19]).

Regarding the coefficient of free charge recombination, it is well established that γ is determined by the capability of the CT state to reform free charges in competition with its decay to the ground state; a large reduction factor (close to unity) indicates inefficient CT resplitting and vice versa [43], as clearly shown in Fig. 2(b). While different $\eta_{d,CT}$ values can reproduce certain individual γ_{meas} data points, they do not provide a consistent description across the entire data set.

A systematic dependence of γ on ΔE_{LE-CT} is, indeed, expected from the energy-gap law: a larger (more positive) ΔE_{LE-CT} implies a smaller CT energy and consequently

a higher CT decay, which would decrease $\eta_{d,CT}$ through Eq. (2b) and correspondingly increase γ . However, the opposite trend is observed experimentally. A recent publication has reported an increase of $k_{f,CT}$ for decreasing offset, which was attributed to an increasing coupling of the CT1 to a short lifetime LE [36]. Figure 2(b) indeed shows that the experimental γ values are well reproduced by increasing the CT lifetime as the energy offset decreases (a reduction in $\eta_{d,CT}$), with the bold line representing $\Delta E_{LE-CT} \approx 0$ and the lightest line corresponding to $\Delta E_{LE-CT} \approx 0.15$. On the other hand, significantly increasing $k_{f,CT}$ to explain the large γ_{meas} for our small-offset systems decreases η_{CG} and η_{PL} well below experimental values, meaning that this approach is not appropriate (see Fig. S2(a) in the Supplemental Material [19]).

Alternatively, $k_{d,CT}$ could be altered for a similar effect. For example, a recent work has shown the Langevin reduction to be strongly related to the quadrupole moment of the NFA due to band bending [44]. As band bending also reduces the LE-CT splitting [8], a correlation between γ and ΔE_{LE-CT} via a systematic change of $k_{d,CT}$ may be plausible. However, a reduction of γ with decreasing offset is expected from these considerations, in contrast to the experimental findings. Also, as in the previous approach, a consistent explanation of all four metrics is needed here, but is not possible due to the dependence on the CT dissociation efficiency. Notably, η_{EL} (and η_{PL}) is currently independent of $k_{d,CT}$ because all dissociated charges reform to CT, thereby not changing the LE-CT balance.

To conclude this section, we find that both the 2-state and 3-state models, which consider only singlet local excitons and CT states, adequately reproduce the experimental IGE and PLE data. However, they completely fail to capture the underlying recombination pathway of the ELE or γ .

C. The triplet CT (the 4-state model)

It is unsurprising that the 3-state model is inadequate at describing recombination in OSCs, as only one out of four free charge encounter (i.e., spin uncorrelated) events form singlet CT states, while the remaining 75% populate the triplet CT state [45]. This CT3 is characterized by both a redissociation to CS (equal to that of CT1: $k_{d,CT3} = k_{d,CT}$) and, in a first-order approximation, a constant decay rate coefficient $k_{f,CT3}$. With this, the CT3 is added as an additional (non-radiative) decay channel.

Under these assumptions, the dissociation efficiency of the CT3 state becomes the new free parameter in the 4-state model used to fit the data and is defined as

$$\eta_{d,CT3} = \frac{k_{d,CT3}}{k_{d,CT3} + k_{f,CT3}}. \quad (13)$$

The impact of $\eta_{d,CT3}$ on the LE decay efficiencies is similar to the impact of $\eta_{d,CT}$ (see Fig. S2 in the Supplemental Material [19]). It is evident that the two variables are connected: with complete CT3 dissociation, and thereby no CT3 decay, all free charges eventually reform through CT1. However, for smaller $\eta_{d,CT3}$, charges are lost through CT3 and do not redissociate into CS, reducing the reformation to LE considerably, just as a larger $k_{f,CT}$ does. Interestingly, the case $\eta_{d,CT3} = 0$ (the darkest lines in Fig. 3(a)) does not predict γ to be one. The reason is that 25% of charge encounters populate CT1 which, due to their rapid resplitting, reduces recombination.

Figure 3(a) shows how at higher CT3 dissociation efficiencies, charges undergo multiple cycles of recombination and redissociation, leading to a reduction in γ . The impact of $\eta_{d,CT3}$ on γ is distinct, in that it affects the entire driving-force range, whereas $\eta_{d,CT}$ primarily acts on the positive offset, where LE dissociation is efficient (Fig. 2(a)). Still, the 4-state model, with only a constant CT3 decay rate coefficient, remains inadequate at recreating the Langevin reduction factor. A comparison between the experimental data and the different $\eta_{d,CT3}$ cases in the 4-state model (Fig. 3(a)) provides insight into how incorporating a *variable* CT3 dissociation efficiency can improve agreement with experimental observations. This model suggests a sharp transition in $\eta_{d,CT3}$ at low energy offset. Specifically, a low $\eta_{d,CT3}$ (the darkest line) for $\Delta E_{LE-CT} \lesssim 0$ eV, which quickly transitions to a high $\eta_{d,CT3}$ (the lightest line) for $\Delta E_{LE-CT} \gtrsim 0.1$ eV, would capture the behavior of the Langevin reduction factor. Since the CT3 dissociation rate coefficient is assumed to be constant, in line with that of CT1, we require a variable CT3 loss pathway to establish such a new transition.

D. The triplet excitons (the 5-state model)

Here, it is natural to adopt a Marcus framework (Eq. (11)) to populate localized triplet excitons through the recombination of CT3 states. The direct decay from CT3 to S_0 is replaced by triplet formation, $k_{f,CT3} \rightarrow k_{r,T}$, such that the spin-forbidden CT3 decay is removed from the model. The redissociation $k_{d,T}$ of the triplet to CT3 [12] is also modeled according to Marcus theory, while the triplet decay $k_{f,T}$ is treated as a constant value. The dissociation efficiencies of the triplet exciton and CT3 are obtained analogously to the singlet branch (Eqs. (2a) and (2b)):

$$\eta_{d,T} = \frac{k_{d,T}}{k_{d,T} + k_{f,T}}, \quad (14a)$$

$$\eta_{d,CT3} = \frac{k_{d,CT3}}{k_{d,CT3} + k_{r,T}^{\text{eff}}}, \quad (14b)$$

where $k_{r,T}^{\text{eff}} = [1 - \eta_{d,T}]k_{r,T}$. In contrast to Eq. (13), $\eta_{d,CT3}$ is no longer constant and allows for the new sharp transition in γ , as described in the previous section. This transition

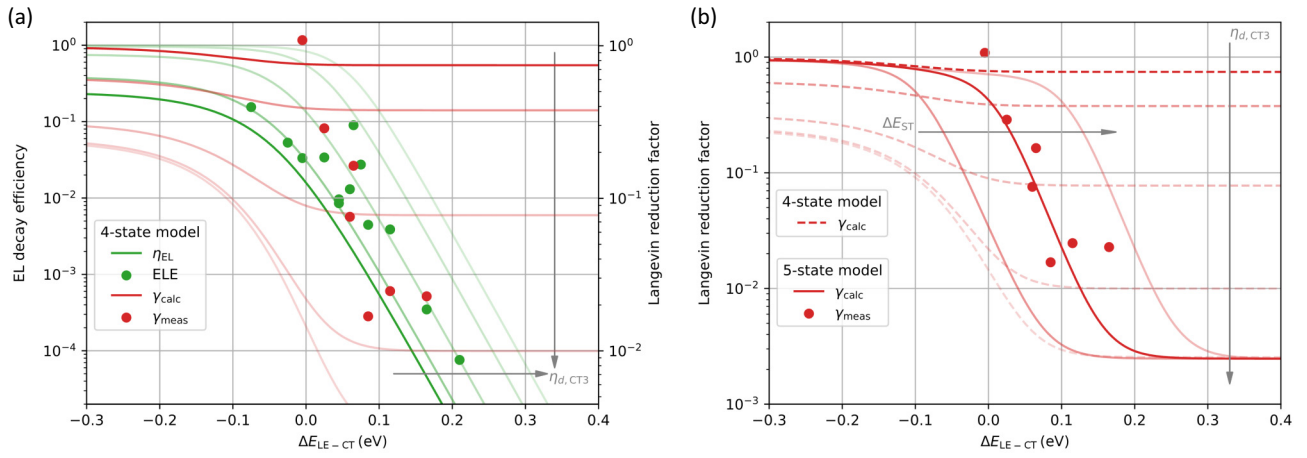


FIG. 3. Including localized triplets unlocks simultaneous description of recombination via ELE and γ . (a) The Langevin reduction factor λ_{calc} and η_{EL} calculated in the 4-state model with increasing CT3 dissociation efficiencies $\eta_{d,CT3}$ (%) = 1, 50, 90, 99, and 99.99 as indicated by the arrows. The same curves are shown dotted in the next panel. (b) The Langevin reduction factor calculated in the 5-state model (solid lines) for increasing singlet-triplet offset ΔE_{ST} (meV) = 200, 300, and 400 meV as indicated by the arrow. The triplet exciton formation and dissociation are modeled as Marcus transfer rates, allowing the model to reach higher $\eta_{d,CT3}$ values at increasing offset.

is manifested by the competition of the formation and dissociation of the triplet, mirroring the LE competition already seen in the 2-state model. This LE competition already affects the Langevin reduction (Figs. 2(a) and 3(a)), creating an early transition starting around $\Delta E_{LE-CT} \approx -0.1$ eV. The new transition stemming from the competition on T is expected to occur at a different energy $\Delta E_{LE-CT} \approx +0.1$ eV to follow the experimental data—a shift of some hundreds of millielectronvolts.

In this context, incorporating localized triplet excitons naturally satisfies both conditions:

- (1) the energy shift relative to the singlet competition given by the singlet-triplet energy difference ΔE_{ST}
- (2) the variable rate or competition through the offset-dependent triplet formation and dissociation rates via Marcus theory

For small offsets, the CT energy lies close to that of the LE and is therefore much higher than that of the triplets. Thus, the formation of triplets (upon recombination of CT3) is highly efficient, while their redissociation is hindered by an energy barrier of roughly ΔE_{ST} . In this picture, the triplets act solely as a dead-end recombination channel, an equivalent picture to the 4-state model with $\eta_{d,CT3} = 0$ (Fig. 3(a), dark line) where all CT3 recombine to S_0 ; either directly in the 4-state model or via triplets in the 5-state model. As the CT energy decreases (higher ΔE_{LE-CT}), the triplet redissociation rate coefficient increases to the point where the triplet decay channel is no longer viable ($\eta_{d,T} = 1$). At this point, CT3 states fully redissociate into free charges, with $\eta_{d,CT3} = 1$ (Fig. 3(a), lightest line). The model sharply transitions between these two extremes.

This directly correlates with γ through the following equation (derived from Eq. (S6.5), in the Supplemental Material [19]):

$$\gamma = \left[\frac{1}{4}(1 - \eta_{d,CT}) + \frac{3}{4}(1 - \eta_{d,CT3}) \right], \quad (15)$$

which expresses the suppression of charge recombination relative to the Langevin limit in terms of the redissociation efficiencies of singlet and triplet CT states, $\eta_{d,CT}$ and $\eta_{d,CT3}$. Note that $\eta_{d,CT3}$, and therefore γ , are heavily influenced by triplet kinetics through Eq. (14): higher triplet redissociation (or suppressed triplet formation) correlates with reduced recombination (cf. Ref. [26]).

Figure 3(b) showcases the Langevin reduction factor, where a singlet-triplet offset of 300 meV—a reasonable estimate for state-of-the-art NFAs [38]—creates a transition aligning well with the data. Note that the Marcus rate coefficients exhibit a turning point in the Marcus-inverted regime. This behavior predominantly lies outside of the calculated data range due to the relatively high reorganization energy ($\lambda = 550$ meV), such that $|\Delta E_{LE-CT}| \leq \lambda$ and even $|\Delta E_{T-CT}| \leq \lambda$. For much smaller values of λ , the effect becomes noticeable (see, e.g., Fig. S7(b) in the Supplemental Material [19]) but can be readily rectified by setting the rate coefficients in the inverted Marcus region to a constant value. An extension to the Marcus-Levich-Jortner model (see, e.g., Ref. [31]) would provide a more physically rigorous description of the rate coefficients. Nonetheless, within the range of offsets considered here and neglecting temperature dependence, the simple Marcus formulation (along with a constant inverted regime,

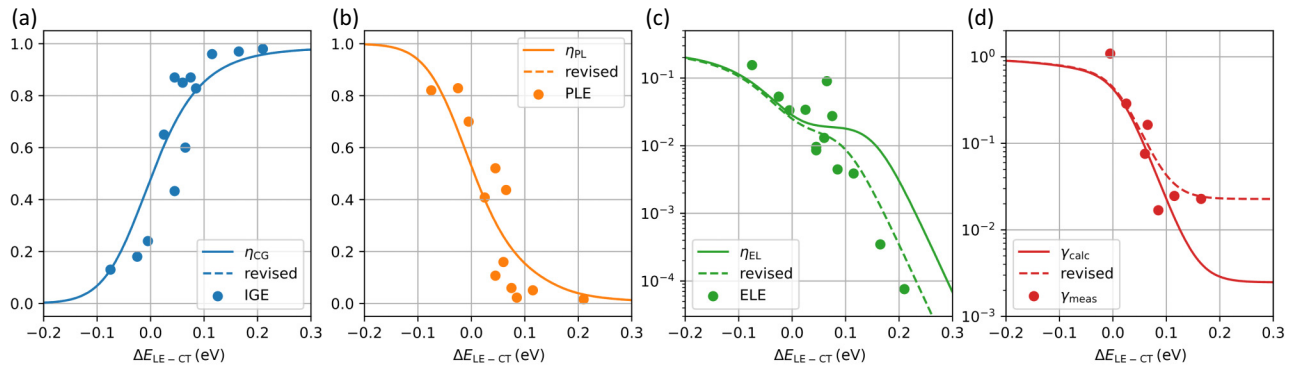


FIG. 4. CT state revisions refine key metrics, improving on the simple model. The (a) free charge generation efficiency, (b) PL decay efficiency (Eq. (4)), (c) EL decay efficiency (Eq. (5)), and (d) Langevin reduction factor. All are calculated in the simple 5-state model (solid lines) as described in Fig. 1 and in the revised 5-state model (dashed lines) where “deeper CT states” are incorporated, i.e., two different CT1 decay coefficients $k_{f,CT} = 10^9 \text{ s}^{-1}$ and 10^{10} s^{-1} are used for the generation and recombination pathways, respectively.

if necessary) serves as an excellent approximation, accurately reproducing the Langevin reduction factor along with the other metrics, as demonstrated in Fig. 4.

E. The EL bump

As previously mentioned, the IGE is unaffected by alterations in the triplet branch, which largely holds for the PL decay efficiency as well. However, the development of a “bump” in η_{EL} is observed around $\Delta E_{LE-CT} \approx 0.1 \text{ eV}$, which does not align with the data (Fig. 4(c), solid line). The offset-dependent triplet formation $k_{r,T}$ has been introduced to allow the model to pass through several different $\eta_{d,CT3}$ values, providing a much better approximation of the measured γ . However, Fig. 3(a) also shows a change of the η_{EL} with $\eta_{d,CT3}$: a lower (higher) CT3 dissociation efficiency implying smaller (larger) electroluminescence, since 75% of injected charges form into CT3 states, significantly limiting the formation of LE. As previously mentioned, $\eta_{d,CT3}$ now increases with offset, such that η_{EL} rises accordingly to form this bump (see also Fig. S3 in the Supplemental Material [19]). The model therefore starts overestimating the ELE for positive offset. In the following, we discuss various approaches to reduce the significance of this bump and improve the model fit.

1. Additional CT3 decay

This could be mitigated, if an upper limit to CS reformation from CT3 existed, realized through an additional decay rate from CT3 directly to the ground state with the rate coefficient $k_{f,CT3}$, causing some charges to be permanently lost through CT3 (in addition to T) and unable to form CT1 states. Figure S6(c) in the Supplemental Material [19] demonstrates how setting $k_{f,CT3} = 10^{10} \text{ s}^{-1}$ almost eliminates the EL bump, which raises the question of whether such a strong decay from CT3 is feasible.

With this coefficient, however, the Langevin reduction factor loses its transition enabled by triplet formation, because $\eta_{d,CT3} \ll 1$. A rate coefficient of $k_{f,CT3} = 10^9 \text{ s}^{-1}$ is the highest CT3 decay possible before compromising on the fit to γ but such a value is unable to remove the bump.

2. Faster CT1 decay

A similar effect can be achieved by increasing the decay of CT1, as it would prevent more electroinjected charges from reaching the LE state (see Fig. S6(d) in the Supplemental Material [19]). However, as part of the singlet branch, the alteration of CT1 heavily influences the generation efficiency as well, causing the upper limit $\eta_{CG,max} = k_{d,CT}/(k_{d,CT} + k_{f,CT})$ to reduce (which was previously very close to unity, due to $k_{f,CT} = 10^{-2}k_{d,CT}$). Figure S6 in the Supplemental Material [19] further illustrates the impact of the various model parameters on the device metrics. The complex interdependencies make resolving the EL bump without affecting the other metrics difficult in the current model.

3. CT energetic disorder

A way out of this problem is to assign two different CT1 decay rate coefficients to the generation and recombination routes. This can be rationalized by considering inhomogeneous energetic disorder, which broadens the density of states (DOS) of the (electronically and vibrationally relaxed) CT states. Because of this, CT1 states formed by exciton dissociation might be of higher energy than those reformed upon free charge encounter.

Exciton dissociation is expected to occupy states higher in the CT1 DOS, especially for positive ΔE_{LE-CT} , where the center of the LE DOS is at higher energies than that of CT1. In addition, photogenerated excitons have fairly short lifetimes, especially in D:A blends, rendering their equilibration into states deep in the LE DOS less likely.

Finally, recent work has found the LE DOS to be on the order of 30–40 meV [46], which is much smaller than that of the charge-transporting DOS from which the CT DOS is derived [47,48]. Note that this concept of energetic disorder is very different from the model of hot CT formation and splitting [49,50]. Here, LE dissociation populates vibronically excited CT states, which are more delocalized and split more easily.

It has been concluded that steady-state charge recombination mainly proceeds among fully equilibrated charges [51,52], at least at or near V_{oc} . This in turn will preferentially populate states deep in the CT1 DOS. According to the energy-gap law, such “deeper” states exhibit a faster decay to the ground state, rendering their resplitting into CS more difficult and thus increasing γ . On the other hand, states at higher energy are more likely to undergo repeated recombination and separation events, compared to the deeper states [53]. The important role of such states on recombination has been proven in a recent study on a wide selection of D:A blends, where a broader DOS led to a larger γ [54], through which k_2 being sensitive to energetic disorder [47] can be easily understood.

This allows us to use two distinct CT1 decay rate coefficients, $k_{f,CT} = 10^9 \text{ s}^{-1}$ and 10^{10} s^{-1} , for photoexcitation and electroinjection, respectively. This is only a slight modification of the model, as all state-population equations can be expressed in the form $n_x = aG_{LE} + bG_{CS}$ to separate the charge generation and recombination pathways (see Note S2.5 in the Supplemental Material [19]). Figures 4(a)–4(d) (dashed lines) visualize the reduction of the EL bump in this revised model without compromising the other device metrics, especially η_{CG} or γ .

IV. RESULTS OF THE 5-STATE MODEL

It is now well established that state models based solely on the singlet branch cannot simultaneously describe all four metrics as a function of energy offset at the D:A heterojunction. Omitting triplets from these models leads to an incomplete representation of the solar-cell energetics and kinetics, especially free charge recombination as reflected by the Langevin reduction. By contrast, our 5-state model accurately captures the device characteristics when utilizing experimentally observed energy levels, reorganization energies, dissociation rate coefficients, and lifetimes, as summarized in Table I (note that the inclusion of “deeper CT states” from the previous section is not addressed in the table).

It is important to recognize that fitting an entire data set—comprising many materials and combinations—with a single set of parameters presents inherent challenges. Naturally, we do not expect one fit to capture the complexity of all material systems. This is evident in Fig. S6(h) in the Supplemental Material [19], where two different H_{ab} values, 10 and 5 meV, fit the IGE and PLE data better

than a single value; and similarly for λ in Fig. S6(g) in the Supplemental Material [19].

A. Competition between charge generation and exciton decay

Figures 2 and S1 in the Supplemental Material [19] illustrate how charge generation competes with singlet exciton decay, with $\eta_{CG} + \eta_{PL} \approx 1$ as discussed earlier. This competition arises from rapid CT dissociation relative to CT decay. Several factors, such as λ , H_{ab} , and $k_{f,LE}$ (see Fig. S6 in the Supplemental Material [19]) simultaneously influence the shape of both curves, maintaining the competition. However, as shown in Figs. S6(d) and S6(e) in the Supplemental Material [19], relaxing the condition $k_{d,CT} \gg k_{f,CT}$ decouples the PLE and IGE. Interestingly, the triplet kinetics can also affect the coupling, e.g., by increasing the CT1 reformation through enhanced triplet dissociation by decreasing ΔE_{ST} or $k_{f,T}$ (see Figs. S6(a) and S6(b) in the Supplemental Material [19]).

B. The role of triplet lifetime

The exact triplet lifetime value has little influence on the fit because the parameters $k_{f,T}$ and ΔE_{ST} produce nearly identical effects on the evaluated metrics (see Figs. S6(a) and S6(b) in the Supplemental Material [19]). Thus, an increase (decrease) in the lifetime can be offset by a corresponding increase (decrease) in the singlet-triplet gap, allowing different combinations of triplet parameters to yield very similar results. This is illustrated in Fig. S7(c) in the Supplemental Material [19], comparing the sets $(k_{f,T}, \Delta E_{ST}) = (10^6 \text{ s}^{-1}, 300 \text{ meV})$, $(10^5 \text{ s}^{-1}, 350 \text{ meV})$, and $(10^7 \text{ s}^{-1}, 250 \text{ meV})$. Diffusion limitation on triplets, i.e., $g(CT3)/g(T) < 1$, can similarly affect the results.

Figures S7(a) and S7(b) in the Supplemental Material [19] further show that variations in the triplet reorganization energy (λ_T) and coupling strength ($H_{ab,T}$)—where triplet formation and dissociation are calculated with different values from that of the singlet processes—have little effect on the model results. This insensitivity allows us to use the simplifications $\lambda_T = \lambda$ and $H_{ab,T} = H_{ab}$ but introduces considerable uncertainty in these parameters as well.

C. Triplet population and non-radiative losses

Figure 5(a) gives further insight into the role of the triplet lifetime to foster recombination and to introduce non-radiative losses. The highest triplet population (under illumination) is found in systems with moderate offset, $\Delta E_{LE-CT} \approx 0.1 \text{ eV}$, due to high LE dissociation and simultaneously low T dissociation at this offset (shown in the middle panel of Fig. 5(c)). The triplet population almost reaches $n_T^{\max} = G_{LE}/k_{f,T} = 10^{22} \text{ m}^{-3}$, 3 orders of magnitude higher than that of the singlet population

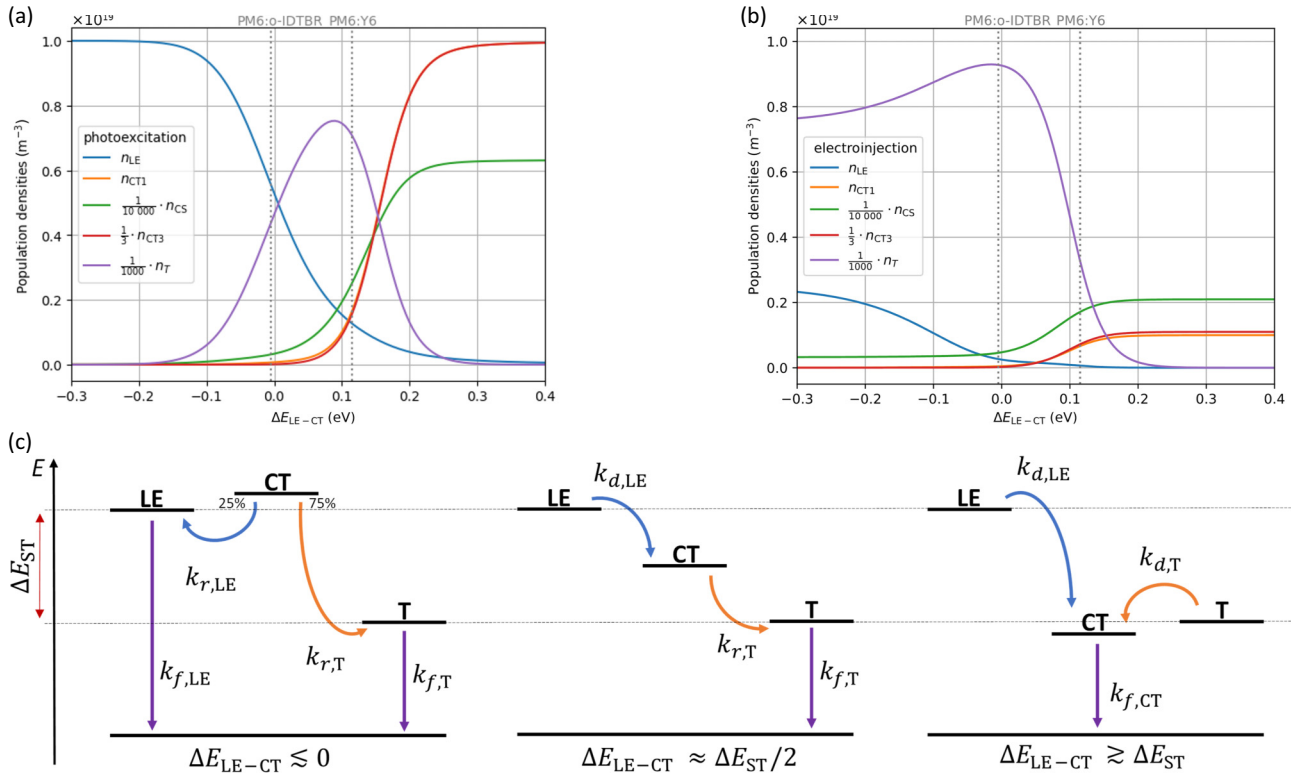


FIG. 5. Revealing the population dynamics and the non-radiative loss channels. Steady-state population densities under photoexcitation (a) or electroinjection (b), modeled in the revised 5-state model; scaled to fit as indicated in the legends. The vertical lines show PM6:Y6 and PM6:o-IDTBR on the energy axis. (c) A simplified diagram of the state model, where CT stands for the degenerate CT1 and CT3, showing only the dominant processes. The triplet population and decay channel become highest for moderate offsets, while high-offset systems are dominated by CT decay.

limit $n_{\text{LE}}^{\text{max}} = G_{\text{LE}}/k_{f,\text{LE}} = 10^{19} \text{ m}^{-3}$, stemming from the lifetimes being $\tau_{\text{T}} = 1000\tau_{\text{LE}}$.

From the triplet state density in Fig. 5(a) (purple), the triplet decay efficiency under illumination can be calculated in accordance with the PL decay efficiency from Eq. (4):

$$\eta_{\text{PL,T}} = \frac{n_{\text{T}}(G_{\text{CS}} = 0)k_{f,\text{T}}}{G_{\text{LE}}}, \quad (16)$$

and vice versa for the triplet decay under electroinjection and Eq. (5). Under steady-state illumination at open circuit, PM6:Y6 (and other systems with the same offset) loses about 70% of excitations through the triplet state. In contrast, PM6:o-IDTBR exhibits only about 40% triplet losses, mainly attributed to less efficient LE dissociation at smaller offset. This trend is in agreement with experimental observations; 90% triplet losses for PM6:Y6 [14] and around 10–30% triplet losses for PM6:o-IDTBR [55] have been found (see also Note S2.9 in the Supplemental Material [19]). Triplet-triplet or triplet-charge annihilation mechanisms are not considered in this model and

can influence the exact value, especially with high triplet populations [56].

Figure 5(b) shows a correlation between the increase of electroluminescence (blue) and the decrease of triplet population under electroinjection (purple) for $\Delta E_{\text{LE-CT}} < 0$. However, due to the 3:1 split of free charge recombination, even at very low offsets where the singlet population reaches its maximum, the triplet population is still very significant. In fact, a maximum η_{EL} of 25% (which is the “singlet loss”) is reached even though the triplet losses make up 75%. Additionally, despite the triplet population quickly dropping at large offset due to less efficient triplet formation and increased triplet redissociation, non-radiative losses do not simply cease to play a role. Rather, the increased CT state population leads to substantial non-radiative losses through the CT1 instead (cf. Ref. [57]). This is visualized in Fig. 5(c), which shows the dominant recombination channel changing with the offset due to the different energetics and subsequent kinetics of LE, CT, and T states. Note that while the non-radiative losses change their origin with offset, dominated by either the triplet or the CT1 state (under illumination also the LE), the total recombination remains constant, as detailed in Eq. (S5.8)

in the Supplemental Material [19]. The presence (absence) of the triplet state therefore does not immediately correlate with high (low) NR losses or low (high) device efficiency. Most modern systems, such as the high-efficiency PM6:Y6, are moderate-offset systems, where the triplets are the primary loss channel.

D. Free charge population

Using a realistic CT formation rate coefficient of $k_{r,CT} = 2.5 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ (from Note S2.8 in the Supplemental Material [19]), the free charge carrier population under illumination can be determined, as visualized in Fig. 5(a) (green). Naturally, it increases with the offset, where singlets and triplets dissociate readily and are (re)formed less efficiently. For two example systems (or offsets), we calculate the free charge population: $2.51 \times 10^{22} \text{ m}^{-3}$ for PM6:Y6 and $2.82 \times 10^{21} \text{ m}^{-3}$ for PM6:oIDTBR. These show excellent agreement with measured values of $2 \times 10^{22} \text{ m}^{-3}$ [4] and $2 \times 10^{21} \text{ m}^{-3}$ [55], respectively. The triplet population reaches values similar to those of the free charge population, in accordance with Ref. [18].

E. Predicting device performance

We now turn to calculating the device efficiency from this model, relating both the open-circuit voltage and short-circuit current density to our metrics via

$$qV_{oc}(\Delta E; E_g) = qV_{oc}^r(E_g) + k_B T \ln\{\text{PLQY}_{\text{PS:A}} \eta_{\text{EL}}(\Delta E)\}, \quad (17a)$$

$$J_{sc}(\Delta E; E_g) = J_{ph}(E_g) \eta_{CG}(\Delta E), \quad (17b)$$

where V_{oc}^r represents the radiative voltage limit of V_{oc} and the non-radiative voltage loss is accounted for by the electroluminescence through η_{EL} , using Rau's reciprocity relation (see, e.g., Ref. [20]). Setting $\text{PLQY}_{\text{PS:A}} \approx 2\%$ leads to an ΔE -independent down-shift of 100 mV. The maximum photocurrent density J_{ph} is converted to the actual J_{sc} by the free charge generation efficiency η_{CG} .

Another major loss in OSCs is the fill factor, which is not addressed directly in this model. There are two main aspects limiting organic FFs: the field dependence of free charge generation and the transport resistance [58,59]. The former is much more pronounced for low $\Delta E_{\text{LE-CT}}$, where the exciton dissociation becomes inefficient as the CT energy is increased with the external voltage. The latter stems from the competition of charge extraction (limited by low mobility) with bimolecular recombination and can be quantified through the figure of merit α , derived in Ref. [60]:

$$\text{FF} = \frac{u_{oc} - \ln(0.79 + 0.66 u_{oc}^{1.2})}{u_{oc} + 1}, \quad (18a)$$

$$u_{oc} = \frac{qV_{oc}}{(1 + \alpha)k_B T}. \quad (18b)$$

We can use our calculated γ as a parameter describing the non-geminate charge recombination in our model, which shows the same trends expected for the field dependence of IGE: quickly increasing for small $\Delta E_{\text{LE-CT}}$. We therefore link the Langevin reduction factor to the figure of merit α to calculate the FF according to Eq. (18). We demonstrate in Note S2.8 in the Supplemental Material [19] how using typical organic solar-cell properties, e.g., $k_2 \approx 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $\mu \approx 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, yields the relation

$$\alpha^2 = 100\gamma, \quad (18c)$$

providing a nice description of the fill factor. High FFs are therefore achieved for $\gamma \leq 10^{-2}$ ($\alpha \leq 1$), which is reached for high-offset systems (Fig. 4(d)). A small reduction in recombination is already seen in well-phase-separated systems such as PM6:Y6, and many other blends that use well-aggregating NFAs (e.g., due to their fluorination), as a result of the geometric confinement of electrons and holes within their respective phases [43,61].

The theoretical efficiency limits of solar cells are calculated in the Shockley-Queisser picture by modeling the Sun as a black body [62], emitting a spectral photon flux density (Fig. 6(a), solid blue line) of

$$\phi_T^{bb}(E) = \frac{2\pi E^2}{h^3 c^2} \left[\exp\left\{\frac{E}{k_B T}\right\} - 1 \right]^{-1}. \quad (19)$$

The photon flux density above the band gap is then

$$\Phi_{bb}(T) = \int_{E_g}^{\infty} \phi_T^{bb}(E) dE, \quad (20)$$

whereby the dark saturation and maximum photocurrent density, assuming absorption of 0% below and 100% above the band gap, are expressed as

$$J_{\text{sat}} = q\Phi_{bb}(T_c), \quad (21a)$$

$$J_{ph} = q\theta\Phi_{bb}(T_s), \quad (21b)$$

with the temperature of the cell $T_c = 300 \text{ K}$ and of the Sun $T_s \approx 6000 \text{ K}$. The contribution of the Sun is reduced by its angular size as seen from Earth, $\theta = (R_{\text{Sun}}/d_{\text{Sun-Earth}})^2$, with the Sun's radius $R_{\text{Sun}} = 6.957 \times 10^8 \text{ m}$ and its distance to Earth $d_{\text{Sun-Earth}} = 1.496 \times 10^{11} \text{ m}$, resulting in the (theoretical) AM0 radiation with a total incident power of $P_{\text{inc}} \approx 1.5 \text{ kWm}^{-2}$, through

$$P_{\text{inc}} = \theta \int_0^{\infty} \phi_{T_s}^{bb}(E) E dE. \quad (22)$$

The measured AM1.5G solar spectrum (Fig. 6(a), dotted blue line) shows only small differences to the black-body prediction—mainly the signal reduction from atmospheric absorption bands and Rayleigh scattering at

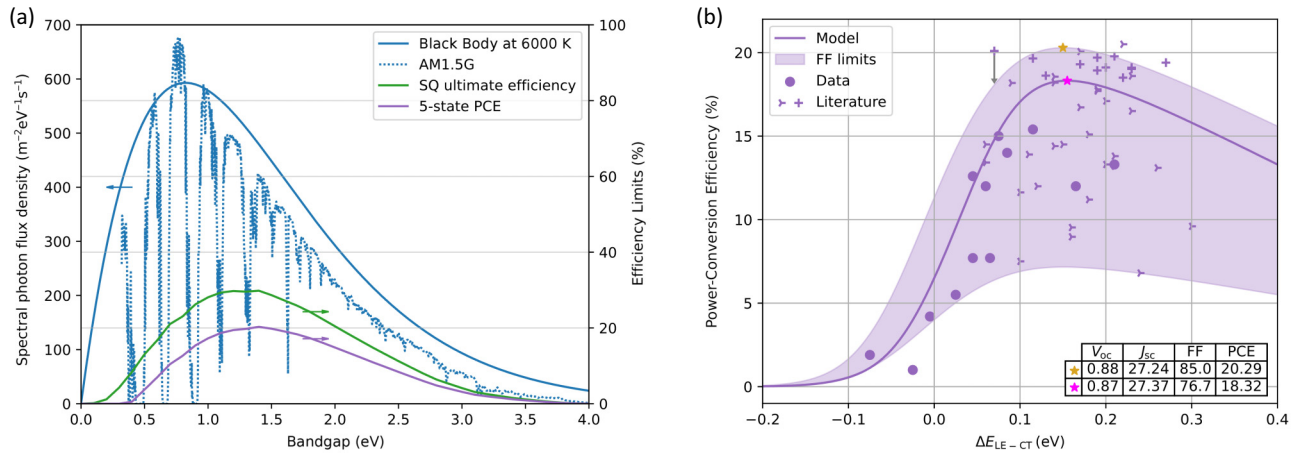


FIG. 6. Model calculations closely match experimental PCEs and reveal the efficiency limits of OSCs. (a) The black-body spectrum of the Sun at $T_s = 6000$ K (solid blue line) and the measured AM1.5G solar spectrum (dotted blue line). Data source: U.S. Department of Energy (DOE)/National Laboratory of the Rockies (NLR)/Alliance for Energy Innovation, LLC (ALLIANCE). The Shockley-Queisser (SQ) ultimate efficiency (green) and the efficiency limit in the 5-state model (purple) are shown. (b) The change in the device efficiency with energy offset ΔE_{LE-CT} for an optical band gap of $E_g = 1.4$ eV, an absorption of 90% above the band gap, and FF according to Eq. (18) (solid line), as well as between 85% and 30% (shaded area) with the maxima marked (stars). Literature values (from Tables S2 and S3 in the Supplemental Material [19]) are shown to complement our data (triangles and plus signs), plotted for ΔE_{HOMO} due to the lack of ΔE_{LE-CT} data. An arrow indicates where a particular outlier falls without the enhanced surface roughness that boosts its light harvesting (LBL, 20.1%), corresponding to the BHJ of lower efficiency (18.4%).

higher electronvolt values. The photocurrent is calculated using AM1.5G to accurately describe real-world solar-cell parameters.

Applying Shockley's equation for an ideal solar cell (see, e.g., Ref. [63]),

$$J(V) = J_{ph} - J_{sat} \left[\exp \left\{ \frac{q}{k_B T} V \right\} - 1 \right], \quad (23)$$

the radiative voltage limit is calculated as

$$qV_{oc}^* = k_B T \ln \left(\frac{J_{ph}}{J_{sat}} + 1 \right). \quad (24)$$

J_{ph} and V_{oc}^* provide upper bounds to J_{sc} and V_{oc} under 1-sun illumination (see Eq. (17)). Figure S9(a) in the Supplemental Material [19] explores their behavior for varying band-gap energies E_g and different absorption bandwidths ΔE_{abs} . Notably, J_{ph} exhibits a stark dependence on ΔE_{abs} up to about 2 eV, after which J_{ph} approaches the theoretical limit.

Figure 6(a) illustrates two different solar-cell efficiencies: first, the Shockley-Queisser ultimate efficiency (green), where the photocurrent is supplied as described in Eq. (21b) (under AM1.5G) and the efficiency is determined from the maximum power point of the J - V curve (Eq. (23)), reaching an efficiency of 33.4% at $E_g = 1.34$ eV; and, second, the calculated 5-state model efficiency (purple), as described in the following.

Using the V_{oc}^* and J_{ph} values from Fig. S9(a) in the Supplemental Material [19] (with an absorption of 90% above

the band gap), the model device efficiency

$$PCE = V_{oc} J_{sc} FF \quad (25)$$

can be calculated for different acceptor band gaps and driving forces. Figure 6(b) shows the experimental data range very nicely recreated by this calculation (solid line). In addition, a collection of literature values for PCEs of D:A blends (see Tables S2 and S3 in the Supplemental Material [19]) is shown to fall almost completely into the calculated PCE range between the fill factors of 85% and 30% (shaded area). These values seem to be the upper and lower limits of organic fill factors through Eqs. (18) when using typical device parameters for OSCs (see Fig. 2 in Ref. [60]).

The PCE curves reveal that the most favorable combination of device parameters can yield a PCE of roughly 20% at an optical band gap (of the acceptor) of $E_{g,A} = 1.4$ eV, with a driving force of $\Delta E_{LE-CT} \approx 100 - 200$ meV. The donor material should have complementary energetics to maximize the combined absorption of the blend, aiming for $\Delta E_{abs} \geq 2$ eV, but is otherwise defined through its HOMO level and the resulting ΔE_{LE-CT} . Charge mobility, which plays a significant role in extraction efficiency and FF, as well as the proper blend morphology to enable charge generation are, of course, essential but not considered in this model directly.

Figure S8 in the Supplemental Material [19] illustrates how the efficiency of our model varies with different considerations for the CT state. Figure S8(a) in the Supplemental Material [19] shows the simple 5-state model,

disregarding the “deeper CT state” that we have introduced to resolve the EL bump. Maintaining the same CT decay ($k_{f,CT} = 10^9 \text{ s}^{-1}$) for both photoexcitation and electroinjection results in an increased η_{EL} and consequently an enhanced PCE, particularly for $\Delta E_{LE-CT} > 0.1 \text{ eV}$, reaching a maximum of 21.4%. Figure S8(b) in the Supplemental Material [19] looks at the PCE curve if we introduce a CT dissociation that reduces for low offsets, as proposed in Ref. [2]. This is discussed further in Note S2.12 in the Supplemental Material and the metrics are shown in Fig. S5 in the Supplemental Material [19]. It is only noticeable for $\Delta E_{LE-CT} < 0.1 \text{ eV}$, where the efficiency is decreased slightly—leaving the maximum PCE unchanged. These two adjustments show how the simple 5-state model can approximate the experimental PCE data, and therefore is a viable model for modern OSCs, while some CT modifications offer valuable improvements.

V. OUTLOOK

Our model predicts the PCE of OSCs to be limited to slightly above 20%, which fits nicely with recent record efficiencies for binary blends (see Fig. S10 in the Supplemental Material [19]). This limit, it should be reiterated, is not an inherent limit to OPVs but stems from the characteristics of modern polymer-donor:NFA binary BHJs. Fullerene devices, for example, are not fitted with these parameters and a different generation of materials could exhibit different behavior and exceed this limit.

Analysis of the parameter effects on the model results reveals several possible approaches to increasing this PCE limit, especially for low-offset systems (see Fig. S6 in the Supplemental Material [19]). This section explores these approaches, with the maximum PCE found to be increased substantially (summarized in Fig. 7).

A. Triplet excitons

The reduction of ΔE_{ST} , e.g., through increased end-group $\pi - \pi$ stacking [38], changes the balance of triplet dissociation and formation, decreasing the non-radiative triplet losses and the Langevin reduction factor through higher triplet exciton and therefore CT3 redissociation (Eq. (15)). This could, e.g., be achieved through the hybridization of T1 and CT3 [14]. Charge up-conversion through triplet-triplet annihilation is additionally affected by the crystallinity of the NFA domains and can become a relevant effect for longer triplet lifetimes $\tau_T \gtrsim 1 \mu\text{s}$ [56]. Triplet dynamics can improve the FF of an OPV and reduce voltage losses by tens of millielectronvolts, especially at low offset. A slight increase of J_{sc} can be expected through lower triplet recombination, but is not seen in our modeled free charge generation pathway.

B. Singlet excitons

A long singlet lifetime is vital for charge generation [9]. The success of the Y6-based devices is partially said to

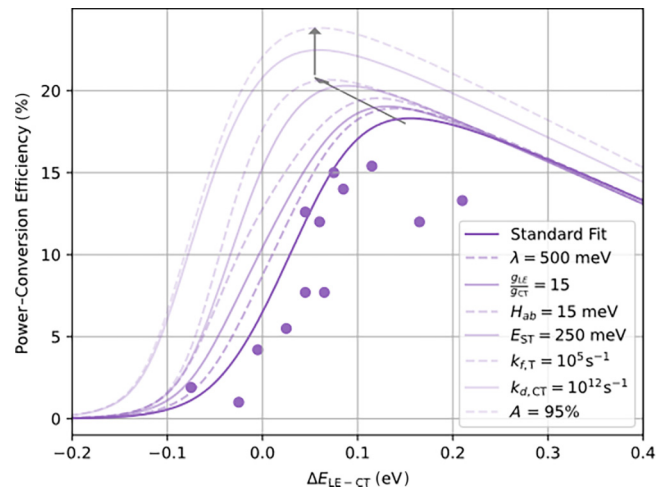


FIG. 7. The increase in the PCE due to small changes in parameters. The “Standard Fit” (the same as in Fig. 6) uses the values from Table I, whereas the other lines continuously change one parameter to increase the PCE. Most have a larger effect at small offset.

come from their molecular packing, shown to be linked to the electronic coupling as well as excited-state reorganization energy [64]. Similarly, singlet exciton losses can be reduced by increased coupling to the donor H_{ab} or reduced reorganization energy λ , e.g., through increased rigidity of the NFA molecule [5]. It may be surprising that these two parameters affect the LE competition (dissociation versus reformation), which is seemingly independent of both:

$$\frac{k_{r,LE}}{k_{d,LE}} = 10 \exp \left\{ -\frac{\Delta E_{LE-CT}}{k_B T} \right\}. \quad (26)$$

However, the *effective* reformation $k_{r,LE}^{\text{eff}}$ is decreased by an increased dissociation efficiency $\eta_{d,LE}$, whereby H_{ab} and λ can indeed have an impact through $k_{d,LE}$. This competition defines the behavior of the IGE and is therefore detrimental to making low-offset systems work. As is evident from Eq. (26), a change in the prefactor can also control the competition through morphology optimization—the prefactor being defined by phase separation and exciton diffusion lengths in BHJs [32]. We finally note that recent efficiency records have used increased exciton generation through light-harvesting methods such as a wrinkled active layer surface [65] or antireflective coating [66].

C. CT states

CT dissociation is already assumed to be efficient compared to its decay [8]. Through Langevin reduction as a measure of CT redissociation, the FF is influenced by the CT dissociation. Additionally, a disruption of the CT dissociation efficiency will heavily impact the IGE and

thereby J_{sc} . Counteracting the low CT dissociation efficiencies as have been proposed for low offset [2] is important to increase low-offset efficiency but will have little impact on the overall efficiency limit.

D. Free charge extraction

Finally, the main limit on the FF in record organic solar cells, where field-assisted LE dissociation is not an issue [59], is set by inefficient charge extraction competing with non-geminate recombination. FFs exceeding 80% are very rare. Recently, a certified FF of 80.5% has been reported for a ternary blend with a PCE of 20% by means of a dual nanoscale fibrillar morphology through a novel NFA [67].

E. Ternary systems

We finally note that certified PCEs close to 21% have been recently reported for ternary blends (see, e.g., Ref. [66]). It is not clear yet what mechanism causes the superior performance of ternary versus binary blends. A recent publication has suggested that adding a third component will give a smaller offset, which may decrease the exciton dissociation rate to a value where the free charge generation is still efficient while the ELQY benefits from less efficient redissociation of LE, thereby increasing the radiative efficiency and reducing the non-radiative voltage loss [20].

VI. CONCLUSIONS

In this work, we have developed an analytical framework that unifies free charge generation and recombination in organic solar cells as functions of the D:A energy offset. We highlight the merits and limitations of models based solely on the singlet branch and show how, by specifically introducing the formation and redissociation of local triplet states, a 5-state model offers the first comprehensive treatment that bridges both singlet and triplet pathways. Our triplet-inclusive model captures not only the IGE and PLQY, but also the ELQY and Langevin reduction factor consistently across material systems. These metrics are tightly linked to the energetics and kinetics of the charge species, including the triplet excitons.

Consequently, our model allows direct estimation of crucial physical parameters, such as the reorganization energy for the CT1-to-LE electron transfer ($\lambda \approx 550$ meV) and the singlet-triplet energy offset ($\Delta E_{ST} \approx 300$ meV). It also reinforces broader concepts, such as the Langevin reduction reflecting CT (re)dissociation or the impact of a broadened DOS on both generation and recombination. Additionally, we extract vital quantities, such as the magnitude of triplet loss or the free charge carrier density. Notably, even in high-performing blends such as PM6:Y6, we find substantial triplet losses, and that a reduction of these does not necessarily correlate with increased ELQY,

due to the competing non-radiative CT decay, especially at high offset.

Furthermore, these metrics enable us to recreate full device characteristics—namely, V_{oc} , J_{sc} , FF , and PCE—supported by SQ-limit analysis and consistent with literature data. We identify key energetic requirements to achieve an optimum efficiency of 20.3% for binary blends, including an acceptor band gap of 1.4 eV, a LE-CT offset of ~ 150 meV (roughly a 350-meV HOMO offset), and complementary absorption of the donor to ensure high photocurrent. These findings explain the observed PCE plateau for binary blends near 20% in recent years, and highlight the need for additional measures, such as increasing the light harvesting, to surpass this limit.

Finally, we propose concrete strategies to push beyond the current efficiency plateau—particularly for low-offset systems—through targeted reductions in the singlet-triplet energy offset, reorganization energy, and domain size, alongside increases in the D-A coupling and absorption strengths. These insights thus provide a practical roadmap toward a next-generation NFA design that could raise the performance ceiling of organic photovoltaics beyond today's limits.

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J.L.-K. performed the analysis and wrote the majority of the manuscript. S.S. and D.N. conceptualized the study and designed the methodology. M.P. provided the experimental data, found in the Supplemental Material [19].

DATA AVAILABILITY

The data that support the findings of this paper are openly available [19]. In addition, this work (Fig. 6) used data provided by the U.S. Department of Energy's National Laboratory of the Rockies (NLR), operated by the Alliance for Energy Innovation, LLC [68].

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