Ternary organic solar cells: Insights into charge and energy transfer processes 🄵 🆂🅲🅸

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ABSTRACT

Recent advances demonstrate the efficacy of ternary strategy in organic solar cells. Such excitement is achieved by synergistic improvement in both charge dynamics and energetics. The third component serves as a bridging unit to systematically optimize the charge migration, exciton lifetime, recombination, and nanomorphology. Primarily focusing on the tactics for addressing energy transfer, charge transfer, and voltage losses, specific relationship between kinetics and energetics evolution has been thoroughly analyzed upon addition of the third component. We propose that the future design should be beyond simply complementing absorption, but rather focus on how the guest molecular could specifically address the charge and energy profile. With fine control of morphology, the maximum potential of ternary blends can be realized toward highly efficient organic solar cells.

INTRODUCTION

Organic semiconductors have gained wide industrial and academic attention due to their low cost, non-toxicity, facile synthesis, flexibility, and transparency.[1–4] As recent progress approaches 20% of power conversion efficiency (PCE),[5–8] emerging insights from molecular physics, synthesis, and device physics demonstrate a promising future for systematically designing highly efficient bulk heterojunction organic solar cells (OSC).[9–11] One of the most effective tactics to boost the efficiency and stability of OSC is achieved via the addition of a third component into the blend.[12–16] With reference to the existing binary mixture, the addition of donor/acceptor third components can energetically and morphologically fine-tune the bulk heterojunction to attain synergistic improvement in short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill-factor (FF), and consequentially, PCE.[17–20] Taking advantage of promising non-fullerene acceptors, the ternary blend can, therefore, extend its absorption capability in the near-infrared (NIR) region.[21–24] Other effort has also been dedicated to optimizing the blend morphological profile through the addition of the third component.[17,25,26] Depending on its preferred location, intermixing profile, and energy level, the ternary blend may operate in different modes.[13,26–31] While an energy cascade mode depicts the energetic downward trend for a charge transfer relay,[32–34] the parallel mode describes the situation where dual charge dissociation channels (donor$_1$–acceptor and donor$_2$–acceptor or donor–acceptor$_1$, and donor–acceptor$_2$) occur simultaneously.[35–37] When the guest molecular exhibits favorable miscibility and similar structure with one of the binary components, the alloy-like model is implemented to investigate energy level shifting and morphological control.[38–41] When designing and selecting the third component, it is pivotal to unravel the specific step-by-step photophysical processes that are potentially impacted upon adopting the ternary strategy. Moreover, in comparison with drastic improvement achieved in J_{sc}, which is mostly attributed to the conducive panchromatic absorption, the disproportionate amount of effort on V_{oc} enhancement withholds the further excitement that could be endowed via the third element. In fact, research revealed that charge dynamics in terms of transport and dissociation largely dominate the resultant J_{sc},[42–45] while V_{oc} is more determined by the energy landscape of the blend.[46–50] In addition to material and microfabrication defects, FF is determined by the competition between recombination and free charges extraction.[51–56] Therefore, reconciling charge behavior with a great energetic profile is the ultimate goal for realizing highly efficient OSC. It is also of paramount importance to point out the inseparable relationship between those two key concerns. While donor–acceptor energy offset may no longer be critical for exciton splitting due to self-stimulated dissociation,[57] the interfacial properties along with molecular orientation still correlate with the charge recombination and contribute to the voltage losses.[58–60] Furthermore, strenuous effort in unveiling the role of sub-bandgap states in charge
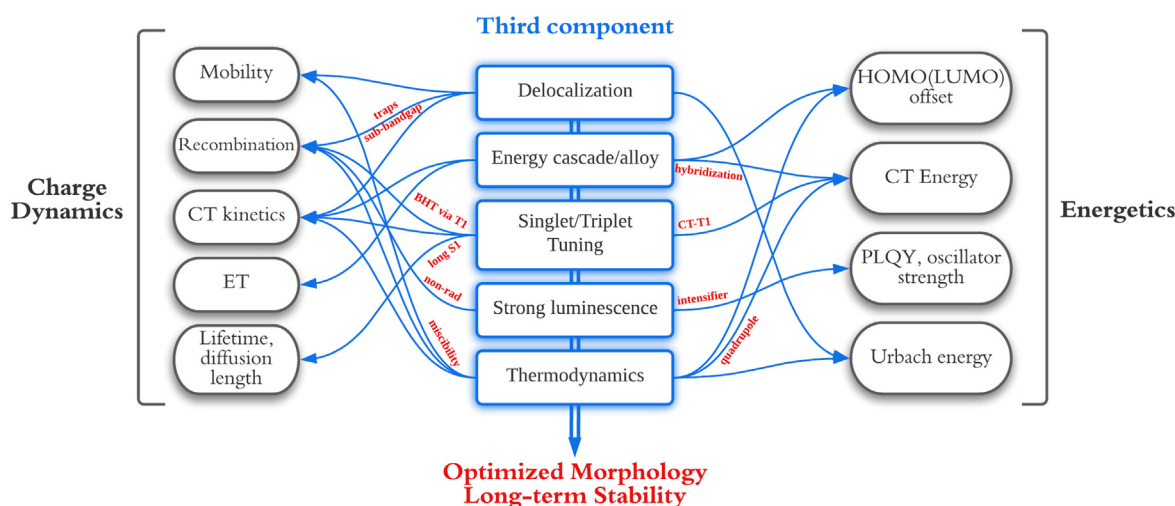
FIG. 1. Schematics of how the third component bridges and relates to charge dynamics and energetics.

dynamics has seen fruitful progress.[61–67] Hence, it is imperative to effectively translate fundamental insights to molecular/material engineering for future applications. With the assistance of a third component (Fig. 1), we envisage to instill more engineering perspective for simultaneously controlling charge dynamics and energetics.

Herein, specific charge behaviors and energy landscape optimization upon the addition of the ternary components are scrutinized. From disentangling charge transfer/energy transfer in the ternary blend to analyzing triplets/mid-bandgap states mitigation endowed by such strategy, the synergistic effect beyond merely complementary absorption is revealed, which further emphasizes and strengthens the potential of ternary organic solar cells (TOPV).

UTILIZING CHARGE TRANSFER AND ENERGY TRANSFER IN TOPV

To efficiently separate tightly bonded exciton in organic semiconductors and compete with the intrinsic relaxation process within the same moiety, charge transfer plays a significant role in achieving high free charge carriers yield. From an energetic point of view, it was widely acknowledged that interfacial energy offset is critical for exciton dissociation, which usually and inevitably compromises the realization of high V_{oc}.[68–71] However, the recent literature revealed that long-lived singlet states/charge transfer (CT) states in non-fullerene acceptors[72–75] and photo-induced bulk polarization,[57] can change this paradigm. While relieving the energetic requirement for exciton splitting, more attention is shifted to engineer exciton lifetime and interfacial CT states. The ternary component, in this regard, can both morphologically and electrically modulate the exciton behavior and retain voltages losses.[25]

An effective strategy to promote charge transfer is to form an energy cascade in the ternary blend. The downward trend of the three components provides a smoother energetic transition to split excitons. The charge transfer rate k_{CT}, according to the classic Marcus theory,[76,77] is defined as

$$k_{CT} = \frac{2\pi}{\hbar\sqrt{4\pi\lambda k_B T}} V^2 \exp\left(-\frac{(\lambda + \Delta G)^2}{4\lambda k_B T}\right), \quad (1)$$

where $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, T is the temperature, V is the electronic coupling between the initial and final states, ΔG is the Gibbs free energy, and λ is the reorganization energy. $-\Delta G$ represents the free energy, which equates to the frontier molecular level difference (ΔHOMO in the case of hole transfer) plus the binding energy. Generally, larger energy offset renders an exponentially higher charge transfer rate.[76] However, the sub-picosecond CT rate has also been recently reported with a negligible driving force,[78] which is conducive to compete with intrinsic decay. Noticeably, the transfer integral can drastically drop if the donor–acceptor interface moves further apart. Therefore, the ternary strategy can morphologically regulate the interfacial environment to mitigate the exciton-diffusion mediated CT process, while promoting delocalization, reducing reorganization energy, and optimizing the electronic coupling to maximize the CT rate.[79,80] Meanwhile, judicious selection of the third component can also facilitate hybridization between CT and local exciton (LE) states,[81,82] which again sheds light on the necessity of obtaining long-lived singlet state to benefit CT kinetics[83] and suppress non-radiative voltage losses (ΔV_{nr}). However, detailed analyses regarding the process and kinetics related to exciton splitting necessitate further investigation. For instance, in the case of cascade mode, the dissociation process could potentially occur not only at donor/third component interface, but also third component/acceptor interface. Therefore, the lifetime and diffusion process of excitons in the moiety of the energetic relay, which is the third element's domain, will be of prime importance. Given numerous negligible HOMO offsets presented in the different ternary blends, it is also energetically possible of achieving thermodynamic equilibrium that can favor back hole transfer and subsequently charge dissociate due to dipolar polarization.[57] Noticeably, the third component can simultaneously obtain different functions within the same blend, which means that the charges can also be potentially extracted at between the two donors or acceptors (in the case of the parallel model). To verify or negate such hypothesis, in-depth analysis and distinguishable

spectroscopic features from transient absorption (TAS) are required to unveil the kinetics of charge (mainly hole) transfer mediated by the third component.

Taking the case of the widely studied P3HT:PCBM blend, Sperlich et al.[84] employed electron paramagnetic resonance (EPR) to examine the electron distribution after the initial transfer from the donor to the two alloy-like acceptors, which are $PC_{60}BM$ and $PC_{70}BM$, respectively. They found out that the frontier orbital energy difference as well as stoichiometry between the original acceptor and the amount of third component of fullerene derivative crucially determines the charge behavior and energetic landscape. Negligible LUMO difference (6–10 meV) between $PC_{60}BM$ and $PC_{70}BM$ further forms intermixed phase, which shrinks the blend's energy offset and eventually promotes the V_{oc} and J_{sc} synergistically. Other reports that the fullerene ternary blend containing PCBM and ICBA can effectively shift the CT energy level.[79,85] However, the improvement of the V_{oc} is attributed to distinctive CT state's contribution to electroluminescence quantum efficiency (EQE) via a parallel model, not by the intuitive alloy model.[86]

While the CT states are crucial for effective exciton dissociation in the case of fullerene, their intricate role in non-fullerene blends is rather elusive and complicated. It was recently summarized that CT lifetime follows a reverse bandgap law for nonfullerene acceptors (NFAs),[74] and long-range charge separation of CT excitons to free charges requires much longer time.[73] Thus, these findings highlight the importance of realizing long-lived and disorder-free CT states. To realize such CT characteristics, barrierless design and choice of donor and acceptor lead to quasi-equilibrium of LE, CT, and charge separate (CS) state.[73] This inevitably leads to the trade-off between exciton dissociation and rapid radiative recombination through singlet states. However, with the assistance of the guest molecules, the compromise of the luminescence quantum yield can be mitigated. In Liu et al.'s work, a highly emissive small molecule IT-MCA is added to the binary blend, which boosts the electroluminescence quantum efficiency (EQE_{EL}) one order of magnitude higher to 8.7×10^{-3}% and reduces ΔV_{nr} to 0.243 V.[87] Given that

$$\Delta V_{nr} = -\frac{kT}{q} \ln(EQE_{EL}), \qquad (2)$$

where k, T, and q denote the Boltzmann constant, temperature, and the elementary charge, respectively. Due to its energy landscape, the wide bandgap IT-MCA serves solely as a fluorescence emitter to suppress the non-radiative voltage losses. Further photoluminescence spectroscopy verifies that such emission intensification is achieved via Förster resonance energy transfer (FRET) (from IT-MCA to acceptor). The same strategy also reveals positive results on the PM6:Y6 blend, which enhances the PCE by 7.7% to 16.7%.[87] Notably, the improvement in J_{sc} is also observed in different negligible-offset non-fullerene blends. Even though FRET does not contribute to the exciton dissociation process, the more ordered face-on orientation upon the third component addition regulates the charge transport and contributes to this synergistic effect.[88]

The utilization of FRET in TOPV demonstrates striking success in improving free charges generation. Apart from luminescence intensifier, it is primarily used to promote rapid long-range migration for enhanced exciton harvesting. Typically, efficient FRET could occur up

to 8–9 nm.[89–93] The key performing parameter, which is the rate, k_{FRET}, is defined as

$$k_{FRET} = \frac{1}{\tau_0}\left(\frac{R_0}{R}\right)^6, \qquad (3)$$

where the Förster critical distance R_0 has the following formula:

$$R_0^6 = \frac{9000\ln(10)}{128\pi^5}\frac{\kappa^2\phi}{n^4 N_A}\int_0^\infty \frac{F(\nu)\epsilon(\nu)}{\nu^4}d\nu, \qquad (4)$$

where κ represents the orientation factor concerning donor and acceptor, R is the distance between the FRET donor and acceptor, τ_0 denotes the fluorescence lifetime of the donor, n is the refractive index, ϕ denotes the fluorescence quantum yield of the donor, N_A is the Avogadro constant, and F and ϵ describe the normalized donor emission spectrum and the acceptor absorption spectrum. Therefore, obtaining a short radiative lifetime of the donor while retaining a long R_0 renders a high FRET efficiency. Notably, the sole consideration of the spectral overlap without morphological control does not lead to direct energy transfer (ET) efficacy improvement,[89,90] which justifies the relatively smaller portion of ET-serving additive in the ternary blends.

To further explore the potential and the synergistic effect provided by such strategy, more specific charge dynamics regarding individual interfaces are yet extensively investigated. It is commonly reported that the exciton dissociation process is unlikely to occur between the energy transfer domains. Nevertheless, the contribution of charge generation from the ET donor and the original acceptor should also be distinguished from the significant increase in J_{sc}. On the other hand, in the case of donor:acceptor$_1$:acceptor$_2$ (D–A$_1$–A$_2$) blends, an acceptor with long exciton lifetime would favor the ET from the highly luminescent wide-bandgap donor.[94,95] Such requirement is also necessary for subsequent exciton splitting if CT instead dominates the interfacial charge dynamics.[96] It is also worth understanding whether charge transfer at D–A$_1$/D–A$_2$ interface (depend on where ET occurs) can compete with high intrinsic radiative recombination to create additional current generation pathways.

It is of paramount importance to highlight that inducing ET in TOPV does not always favor device performance, regardless of morphological impact. For the PTB7:PCBM blend, the incorporation of PDPP2TBT worsens the PCE, which is assigned to the reduced energy offset between the guest molecular and the fullerene.[97] It is important to bear in mind that ET does not directly translate into higher photon-to-current conversion. The determining factor now relies on the efficiency of exciton dissociation at your FRET acceptor and the other material.

The phenomenon of the competition between CT and ET has been extensively reported, where the charge generation yield is compromised by the presence of ET. However, the specific mechanism is not thoroughly investigated, and few remedies have been proposed to mitigate such occurrence. As shown in Figs. 2(a)–2(c), in the case containing fullerene acceptors, the ternary component can facilitate donor/acceptor exciton harvesting or serves as the donor to complete the exciton dissociation relay. In the classic case of P3HT:PCBM, where the two-step process involving the intrinsic FRET from the polymer donor to fullerene domain as with the subsequent hole transfer process was reported,[95,98] it necessarily strengthens the role of hole
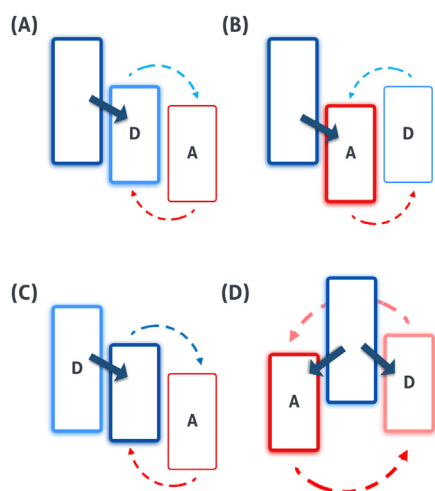
FIG. 2. Schematics of Energy Transfer (ET) occurrence in TOPV. (a) ET between the third component (dark blue) and the original donor; (b) ET between the third component and the original acceptor; (c) ET between the original donor and the third component, and it now serves as the donor in the blend. (d) Dual ET between the third component and the donor as well as the acceptor. Thick arrows represent ET and dashed ones denote charge transfer.

transfer in charge generation. It plays a crucial role, which justifies fullerene's inflexibility to pair with numerous highly luminescent polymers.[99] Benefiting from the long exciton lifetime within the fullerene, such system obviates the need for a large energy offset while maintaining high exciton dissociation efficiency. Therefore, strategy like Fig. 2(a) or 2(b) is highly effective due to (i) ET from the third component with long-lived singlet states in fullerene, (ii) potential intrinsic FRET from the donor to the acceptor, and (iii) complementary absorption with the ternary component. By adding PID2 to the conventional PTB7-Th:PC$_{71}$BM, Lu et al. showed that the ternary blend PCE could be significantly boosted to 9.2%.[100] The intermixing of PID2 and the donor polymer facilitates the efficient FRET process. Moreover, the improved hole mobility, reduced traps, increased available interfaces, and enhanced crystallinity of the fullerene upon the addition of PID2 simultaneously contribute to high J$_{sc}$, V$_{oc}$, and promising FF of 77%. Nevertheless, ultrafast FRET has also proved to be a loss pathway to compete with electron transfer.[99] The root cause is attributed to the insufficient driving energy for fullerene excitons to separate at the interface. Thus, such approach necessitates a considerably large HOMO–HOMO offset, which is at the cost of high V$_{oc}$.

The ET + CT relay also applies in the case of NFAs [Figs. 2(b) and 2(d)], where the third element predominantly promotes the charge evolution through the acceptor. Research proposed that the immediate electron transfer upon photoexcitation precedes ET, which justifies the local dielectric environment changing at the interfaces for the subsequent dissociation process for ET-transferred excitons. Gautam et al.[101] argued that those FRET-mediated excitons require a longer lifetime for retaining efficient separation, which can compete with the intrinsic high radiative recombination within the polymer domain.[99,102] When the ternary approach is implemented, as depicted in Figs. 2(a) and 2(c), such competition is spatially avoided if the third component does not serve any other significant role (i.e., considerate

exciton dissociation also occurs between ET donor and acceptor). No matter whether the third component is preferably located at the donor, acceptor, or interface, this additional pathway for ET is separated from the main charge transfer channel, which mitigates the competing loss pathway mentioned above. In contrast to the case in fullerene, where the ET–CT competition stems from the acceptor's incompetence with hole transfer kinetics, the efficient barrier-less hole transfer process discussed above renders NFA TOPV a powerful candidate to overcome the interplay between J$_{sc}$ and V$_{oc}$. Chen et al. demonstrated that NFA TOPV with intense FRET obtains higher photovoltaic performance than energetically favored fullerene TOPV.[103] They compare P(p-FDBND-2T):PBDTPS-FTAZ:ITIC with PBDTPS-FTAZ:ITIC:PC$_{71}$BM, the former outperforms the latter in terms of J$_{sc}$ albeit less optimized energy landscape, giving it PCE of 11.46%. Noticeably, the dual role played by the wide bandgap third polymer also benefits the V$_{oc}$, which retains the value of 0.9 V in the optimized ternary blend. While in the case of energy cascade, Duan et al. adopted the combination of PTB7-Th:PffBT4T-2OD:IEICO-4F to show the impressive J$_{sc}$ improvement to reach 27.80 mA cm^{-2} (binary—24.82 mA cm^{-2}).[104] The effective energy alignment accompanied by optimal ET synergistically gives rise to the high PCE value of 12.12%. Transferring the same strategy to highly efficient PM6:Y6 blend, Cao et al. recently reported a remarkable 17.54% of PCE adopting a medium bandgap NFA BTIC-EH-2ThBr.[105] The effective long-range ET toward NFA enables excitons to go through an efficient separation process while reducing voltage losses, which is ascribed to the superior EQE$_{EL}$ and long exciton lifetime of Y6.

The versatile energy design of the third component can potentially perplex the energy transfer profile of the blend. By judiciously selecting its emission spectrum, Bi et al. presented that the introduction of PCDTBT to PTB7-Th:ITIC induces dual FRET.[106] Despite energy alignment mismatch with NFA as well as poor charge transport with the donor, the incorporation utilizes ET to harvest the majority of excitons and obtain an average PCE of 7.51%, which is 15% higher than the binary. The favorable enhanced face-on $\pi - \pi$ stacking also contributes to a drastic increase in J$_{sc}$. However, the undesired FF reported in the experiment hinders the progress of such approach. More energetically suitable molecules combined with binary elements with great charge transport profile can systematically benefit from such strategy.

FINE-TUNE THE CHARGE-ENERGY INTERPLAY: THE ROLE OF TRIPLETS IN TERNARY BLENDS

Triplet states are long-lived species that typically obtain lower energy than the singlet states, which may induce losses via non-radiative recombination or rapid triplet-charge annihilation. As recent advances also indicate the mechanism and kinetics involving triplets in realizing long-term stability,[107–114] much research has been devoted to unraveling the role of triplets.[115–118] Since CT state is the center of charge transfer, dissociation, and recombination, its spin profile is, therefore, of prime importance. By decoupling the morphological impact, research has revealed the kinetics of oligomerization (dimerization) in C$_{60}$ induced by black hole/electron transfer (BHT/BET).[119] Such concern is also verified in the promising PM6:Y6 NFA blend, where the non-radiative recombination via triplet states accounts for nearly 90% of the voltage losses. Upon illumination, the photo-generated singlet states will evolve into triplets geminately or

non-geminately. For the former case, prior to exciton dissociation in singlet CT state (^{1}CT), spin-mixing with triplet CT states (^{3}CT) occurs, which is followed by back charge transfer (BCT) toward molecular triplet states (T$_1$). Concerning the latter, the dissociated free charges recombine through the CT state according to the spin statistics, forming a 1:3 ratio of ^{1}CT and ^{3}CT excitons. Then, the BET/BHT will take place subsequently. While both geminate and non-germinate triplets are observed in the fullerene blend, more non-geminate species are accountable for the loss in terms of NFA.

While approach like hybridization between T$_1$ and ^{3}CT,[116] end group $\pi - \pi$ stacking,[120] as well as fluorination,[115] have been implemented to tackle the challenge, ternary strategies to fine-tune the charge and energy landscape also come into the picture. By loading a thermally activated delayed fluorescence (TADF) polymer APDC-TPDA to the PBDB-TF:Y6, Du et al. obtained a remarkable PCE of 16.96%, which is 11.3% higher than the original blend and presents a synergistic boost in all key parameters.[121] TADF's long singlet lifetime, morphological optimization due to preferential location at the interface, as well as beneficial FRET to the donor simultaneously enhance the blend's exciton utilization, charge transport, and energy landscape. Such approach has also been transferred to other NFA/fullerene blends and TADF combinations,[121–123] which all exhibit promising performance improvement and long-term stability. Those promising results demonstrate the generality of adopting TADF as the third component.

To better unveil the charge and energy profile of triplets dynamics upon adopting ternary approaches, detailed Jablonski diagrams regarding different energetic landscapes are depicted in Fig. 3. As the superior singlet property of TADF has been revealed, it is imperative to maximize such advantages. Therefore, loading high bandgap TADF would either promote exciton dissociation through the S$_1$–^{1}CT pathway, or directly separate due to favorable S$_1'$–^{1}CT energy offset. Such combinatory effect will not be available in the case of lower bandgap TADF. More importantly, fine-tuning the emission of TADF, which is widely studied in OLED (organic light emitting diode), can engineer

FRET toward either donor or acceptor to utilize additional excitons further.

We now address the most relevant electronic states that contribute to the detriment of device performance, namely, T$_1$, TADF triplet states (T_1'), ^{1}CT, and ^{3}CT. The back charge transfer rate (BCT) derived from Marcus–Levich–Jortner theory[120,124] is formulated as:

$$k_{BCT} = \frac{2\pi}{\hbar} V^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \sum_{\nu=0}^{\infty} \left[\exp(-S_{eff}) \frac{S_{eff}^2}{\nu!} \right. $$
$$\left. \times \exp\left(-\frac{(\Delta G + \lambda + \nu\hbar\omega_{eff})^2}{4\lambda k_B T} \right) \right], \qquad (5)$$

where $\hbar$ denotes reduced Planck constant, V is the electronic coupling between the two states, λ is the classic reorganization energy, k_B is the Boltzmann constant, T is the temperature, S_{eff} is the effective Huang–Rhys factor, $\hbar\omega_{eff}$ represents the high-frequency vibrational energy, and ΔG is the Gibbs free energy, its absolute value equates to the driving energy. A higher BCT rate endows the system more probability to up-convert the triplets via CT state, which may eventually generate free charge carriers for better photon-to-electron conversion.[50,68,73,116,117] It is worth mentioning that the maxima of the BCT rate is highly dependent on the overall λ, and the exponential relationship indicates that a slight change may lead to a drastic charge transfer profile. Therefore, faster charge extraction and escape from the interface can prevent certain systems from such loss mechanism, which explains the retained device performance in the presence of such energy drain.[125,126] In general, a higher T$_1$ state could suppress the back transfer pathway, which necessarily translates to a narrower S$_1$–T$_1$ energy difference when it comes to material selection and design.[115–117,127,128]

Note that for the case where T_1' of TADF is lower than T$_1$, it will worsen the energy landscape by introducing low-lying triplet states. In fact, the high luminescence yield endowed by TADF will be detrimental for any potential charge transfer from the local exciton state to
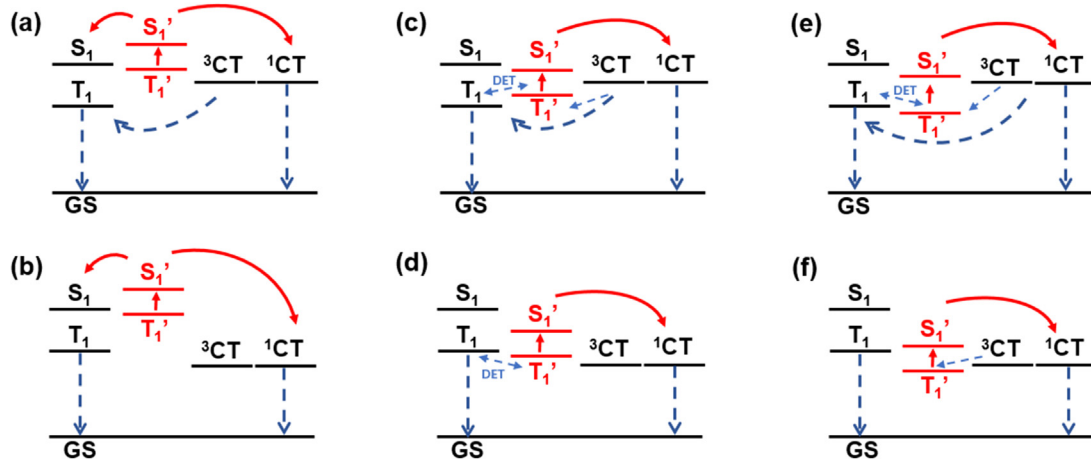
FIG. 3. Jablonski diagram of different TOPV electronic states. (a) $E_{T_1'} > E_{3_{CT}} > E_{T_1}$; (b) $E_{T_1'} > E_{T_1} > E_{3_{CT}}$; (c) $E_{3_{CT}} > E_{T_1'} > E_{T_1}$; (d) $E_{T_1} > E_{T_1'} > E_{3_{CT}}$; (e) $E_{3_{CT}} > E_{T_1} > E_{T_1'}$; and (f) $E_{T_1} > E_{3_{CT}} > E_{T_1'}$. Red arrows denote favorable charge transfer from TADF to either ^{1}CT or S$_1$ state, as well as reverse intersystem crossing (RISC) to promote photon upconversion. Short blue dashed arrows represent potential Dexter energy transfer (DET) and long blue dashed lines depicts fluorescence. $S_{1'}$, $T_{1'}$, and GS denote the third component's singlet state, triplet state, and ground state, respectively.

TADF domain, resulting in high radiative recombination loss. Meanwhile, the proximity of third component with either donor or acceptor can theoretically induce Dexter energy transfer (DET) in which triplet energy can be transferred between different domains.[129] With moderate reverse intersystem crossing (RISC), which is related to spin–orbital coupling (SOC) and S_1–T_1 difference, localized triplets can re-create singlet excitons.[130–132] Considering the relative short distance for such DET event (which occurs within 10 Å), rigorous control of morphology is required to ensure effective phase separation and suppress charge recombination at the interface. However, recent report also presented an endothermic CT-mediated triplet ET process,[133] which enables long-range triplets migration, such excitement might also be insightful for the above proposed singlet-triplet upconversion pathway.

DISCUSSION

Inspired by different charge dynamics and energy landscape optimization endowed by loading the third component, we aim to augment such statement by relating the energetic and kinetic enhancement upon adopting the ternary strategy. As FRET is widely explored to translate the bandgap advantage (complementary absorption and ET) to long-range exciton migration, which intuitively boosts the J_{sc}. It is now crucial to understand its relevance with regard to V_{oc} as well as FF, for which few reports can be able to directly rationalize the enhancement rather than morphological factors.[134,135] The short distance that favors high ET between donor and acceptor inevitably leads to an insufficient distance for effective phase separation, which results in high charge recombination and unsatisfying FF.[94,136] In the meantime, such proximity may also induce molecular orbital wave function overlap and phase match to destabilize/stabilize original electronic states, thus promoting energy bandgap. When the third component's frontier molecular orbital energy level does not lie within the effective binary bandgap, the underlying V_{oc} improvement in the ternary blend remains unclear. Wang et al. assigned the higher FF and V_{oc} to reduced charge recombination, which is due to the reduced interfacial traps upon loading NFA.[137] However, Lami et al.[29] demonstrated that the voltage loss is independent of the material blending ratio. As previous results demonstrate the defect passivation through ternary approach with high mobility polymer,[138–141] they also highlight the critical balance between morphological control and trap profile.[88] Therefore, more insights concerning the location-specific role need to be investigated. The Flory–Huggins model therein reconstructs the phase diagram of the blend concerning thermodynamics:[26,142–146]

$$\frac{\Delta G_{mix}}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + \chi_{12} n_1 \phi_2 + \chi_{13} n_1 \phi_3 + \phi_{23} n_2 \phi_3, \tag{6}$$

$$\chi_{ij} = \frac{\nu_1}{RT} (\delta_i - \delta_j)^2 + 0.34, \tag{7}$$

$$\delta_{i,j} = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}, \tag{8}$$

$$\delta_i \propto \sqrt{\gamma_{sv}}, \tag{9}$$

where ΔG_{mix} is the Gibbs free energy of mixing, R is the gas constant, T is the temperature, n is the number of moles of the molecules, ϕ is the individual proportion to the overall volume, χ_{ij} represents the

Flory–Huggins interaction parameter between those two components. A small χ indicates intimate molecular interaction as well as a tendency to form alloy and less defined phase separation. ν_1 is the solvent volume component, $\delta_{i,j}, \delta_d, \delta_p$, and δ_h denotes solubility, dispersion force, polar force, and hydrogen bonding correspondingly for each element. Last, γ_{sv} is the surface energy, which can be numerically derived through the contact angle at the interface. Such material related model can be well implemented for material scientists to predict the miscibility and morphological preference for efficient charge and energy landscape construction. Revisiting the approach to incorporate high mobility but amorphous donor to the blend, the precise location indeed plays a critical role in harnessing the great charge transport from the guest molecules as well as maintaining robust morphology to suppress charge recombination. The location preference, therefore, determines the subsequent approach for an optimized photophysical process.[147–150] If localized molecular nature and phase separation are preferred, a judicious choice of the pairing element is needed to hinder the energetic disorder. If intensive mixing is favorable, apart from controlling the interface to prevent intense bimolecular recombination, the energy dependency of molecular composition can be exploited to fine-tune the V_{oc}. Moreover, such intimacy may contribute to the formation of percolating pathways, which will be conducive for optimal charge extraction and achieving higher mobility.[151,152] In addition, morphological control can also be achieved via device engineering. Strategies like layer-by-layer deposition to manipulate vertical phase distribution and stacking two binary layers to sequentially cast TOPV are proven effective in fine-tuning molecular interactions, leading to suppressed charge recombination and promisingly high PCE.[153–156] Further insights on the role of morphology to relate optoelectronic properties with charge dynamics and energetics are beyond the scope of this perspective. We, therefore, point out to recent works, which extensively discussed the relevance of domain size, molecular orientation, stacking, crystallinity with energetics and exciton behavior.[157–160]

Kinetics of charge is correlated with each component's energetics. Despite different CT properties presented in NFA and fullerene, the key to charge behavior is the fundamental understanding and identification of the competition of various photophysical events. As discussed above, numerous reports negatively assess the competition between ET and CT. It is mainly because such a highly efficient ET process is not necessarily followed by an efficient CT process, which limits the overall photon-to-electron yield. By selecting suitable energy level alignment to ensure enough driving energy for the case of fullerene, or considering an efficient NFA in which barrier-less charge transfer and exciton dissociation may occur, the ternary strategy provides systematic solutions to address and well-balance the relationship between charge and energy profile. However, as the ternary system tends to complex the energetic profile, and the potential interfacial level shifting induced by quadrupole moments,[161,162] more specific spectroscopic features and simulation[163] need to be established to distinguish the ET contribution from CT, which helps reconstruct the whole picture of charge dynamics.

The competition is also responsible for creating loss channels via triplets. The interplay among the intrinsic relaxation/fluorescence, charge transfer, and intersystem crossing dictates the charge kinetics. Apart from introducing shallow S_1–T_1 TADF to energetically block the BCT pathway, such material could also serve as a delocalization agent to reduce the localized feature of T_1, thus promoting charge

transfer and increasing its probability of dissociation and extraction. In the case of presence of hybridization in the original blend, the third component could also physically enlarge donor and acceptor distance, as well as alter local dielectric environment, which may eventually energetically destabilize the ^{3}CT state and reduce the BCT rate.[116] More excitons can, therefore, be thermally dissociated through ^{3}CT and generate photocurrent.[164] Noticeably, such theoretical advantage is highly dependent on the location of the third component and in-depth understanding its adjacent molecular interactions. Nevertheless, adopting ternary approach could provide alternative strategy to tackle non-radiative loss via triplet states while retaining the hybridization and high luminescence yield of NFA.

CONCLUSION

By revisiting the detailed photophysical process with regard to TOPV, we identified the key feature of the third components as a powerful tool to simultaneously optimize charge dynamics and improve the energetic profile. While complementary absorption is apparently essential, understanding the underlying effect and balance between energetics and charge dynamics can synergistically boost all the figure of merits. With precise control in nanomorphology, a promisingly high PCE is achievable by ternary strategies.

AUTHOR DECLARATIONS
Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Tianyi Zhang: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Writing – original draft (equal); Writing – review and editing (equal). **Nicola Gasparini:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (lead); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review and editing (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article as no data were created or analyzed in this study.

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