Perspective

Controlling the Spin Exchange Energy through Charge Transfer for Triplet State Management in Organic Semiconductors

Alexander J. Gillett,* Richard H. Friend, and David Beljonne*

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Optoelectronic devices fabricated from organic semiconductors, such as organic light emitting diodes (OLEDs) and photovoltaics (OPVs), have reached the point of viability in real-world applications. However, despite the rapid recent progress in the field, open questions remain around the role and management of spin-triplet states in these systems. In this perspective, we discuss recent advances in the manipulation of triplet states, with a particular focus on strategies that involve modulating the spin exchange energy through tuning the degree of charge transfer character in the excited state. We explore the equivalence between the localized and delocalized electronic excited state manifolds in OLEDs and OPVs and propose strategies for aligning the designs of OPVs with those of OLEDs. We consider that lessons from the successful triplet management strategies in the OLED field hold the key for improving the radiative efficiency of OPVs, which is necessary to drive power conversion efficiencies toward the important milestone of 20% and beyond.
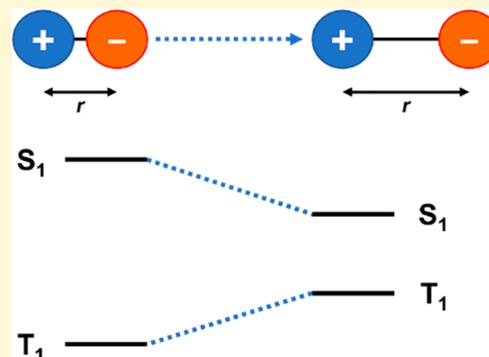
INTRODUCTION

Organic semiconductors show great promise for next-generation optoelectronic applications, such as organic light emitting diodes (OLEDs) and photovoltaics (OPVs).[1−4] However, in contrast to their inorganic counterparts, exciton spin must be carefully considered and successfully managed to obtain device performance suitable for commercial applications. This is because organic semiconductors typically possess a low dielectric constant ($\varepsilon \sim 3-4$), meaning that their primary electronic excitations are Frenkel excitons, where the constituent electron and hole are tightly bound.[5] As such, the spin = 1/2 charge carriers interact strongly, resulting in spin exchange energies typically on the order of hundreds of millielectronvolts.[6] This means that, in most organic semiconductors, there will be spin = 1 triplet excited states below the lowest energy spin = 0 excited singlet state (S_1). However, as the electronic ground state typically has spin-singlet character (S_0), optical transitions between these triplet states and S_0 are formally spin-forbidden.[7] Thus, spin is a key factor controlling the coupling between excitons and photons in organic semiconductors.

The presence of low energy dark triplet states (T_1) in most organic semiconductors has a profound impact on their applications in optoelectronic devices. For example, the spin-statistical recombination of injected electrons and holes into an OLED will result in the formation of 75% dark T_1 states and only 25% bright S_1 states.[8] Thus, the electroluminescence internal quantum efficiency (IQE_{EL}) of an OLED device will be limited to 25% unless steps are taken to utilize T_1 states for light emission. In line with observations in OLEDs, non-radiative recombination of photogenerated charges via the T_1 state is also a dominant loss pathway in many state-of-the-art OPVs.[9−12] As an ideal solar cell should possess only radiative recombination,[13−15] the presence of a significant nonradiative triplet loss channel severely limits performance by reducing the open-circuit voltage from the radiative limit.[9,11] However, the crucial role of triplet states has only recently come to prominence in the OPV community. Prior to the adoption and extensive optimization of nonfullerene electron acceptor (NFA) materials, the power conversion efficiencies (PCEs) of OPVs using fullerene electron acceptors (FAs) were relatively low (∼11%).[16] Thus, despite the widespread observation of triplet recombination in fullerene OPVs,[17−25] the presence of other more substantial loss pathways drew attention away. However, with the PCEs of single junction NFA OPVs, now around 19%,[3,4] attention has turned to identifying those aspects of device operation where significant loss processes remain, including recombination via T_1 states.[9−12]

In this perspective, we focus on recent results for triplet state management strategies in organic semiconductors, achieved
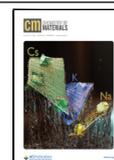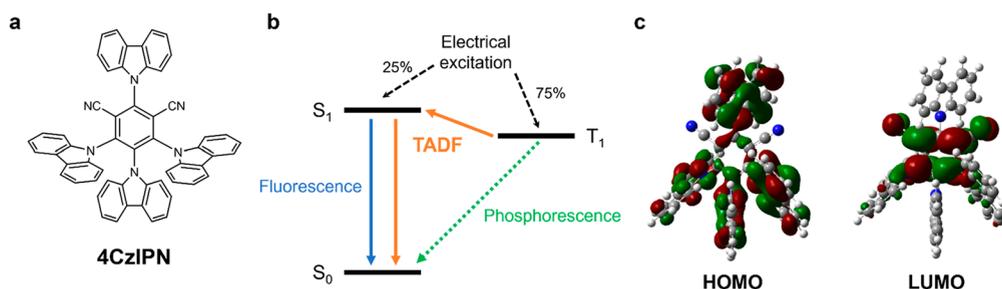
Figure 1. Thermally activated delayed fluorescence. (a) Chemical structure of the archetypal TADF emitter 4CzIPN. (b) Schematic of the TADF process. (c) HOMO and LUMO of 4CzIPN. The HOMO is located on the carbazole donor moieties, while the LUMO is localized on the dicyanobenzene acceptor core.

through controlling the spin exchange energy (J). We consider different designs for engineering the exchange energy through the electron−hole overlap in the excited state, ranging from localized molecular excitations to well-separated charge transfer (CT) states. This allows us to highlight a common thread running through both the OLED and the OPV fields, where significant potential for the exchange of ideas and mutual adaptation of triplet state management strategies exists. Thus, we provide a novel angle for considering triplet state management in these optoelectronic devices.

MODULATING THE SPIN EXCHANGE ENERGY THROUGH CHARGE TRANSFER IN OLEDs

A fundamental breakthrough for triplet state management in OLEDs was achieved by Adachi et al., who provided the seminal demonstration of a highly efficient thermally activated delayed fluorescence (TADF) OLED, as achieved with the archetypal emitter 4CzIPN (Figure 1a). The core underlying principle for TADF is that the energy gap between S_1 and T_1 (ΔE_{ST}; equal to $2J$) should be on the order of the thermal energy available at room temperature (and typically < 100 meV). As a result, the reverse intersystem crossing (rISC) process that upconverts dark triplet states into bright singlets, assisted by ambient thermal energy, can proceed efficiently (Figure 1b). This enables the IQE_{EL} of an OLED to reach 100% as all excited states created after electrical excitation can be used for light emission.[1,26−28]

The most common strategy for achieving a small exchange energy is through designing materials that comprise distinct electron-rich donor (D) and electron-poor acceptor (A) moieties, often further electronically decoupled by a large D:A dihedral angle approaching 90°.[28] This results in the highest-occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) being localized primarily on the D and A segments of the molecule, respectively (Figure 1c). As a result, the lowest energy excited states of TADF materials possess intramolecular CT (intra-CT) character,[29] where rISC is driven by spin−orbit interactions, often involving other triplet states with local exciton character (^3LE) that are in close energy resonance to the intra-CT states.[30−33] We note that an alternative class of TADF molecules known as multiresonant TADF compounds, first introduced by Hatakeyama et al.,[34] also possess a small ΔE_{ST} and show remarkably high singlet radiative decay rates in comparison to conventional TADF emitters (in addition to limited Stokes shifts and narrow emission profiles). This unique combination of properties stems from the peculiar nature of their singlet and triplet electronic excitations, which

involve a short-range redistribution in electronic density,[35] preserving a large oscillator strength while reducing ΔE_{ST} to ∼200 meV; this is small enough for a slow rISC process to take place.

In addition to TADF materials with intra-CT states, efficient rISC can also take place in intermolecular CT (inter-CT) states, where the electron and hole are located on separate molecules.[36−38] This is typically achieved in binary systems consisting of distinct D and A materials that support longer range charge separation. Here, emission occurs through the interfacial CT state, also known as an exciplex. As the exchange energy falls exponentially with distance, ΔE_{ST} rapidly becomes on the order of nanoelectronvolts when the electron−hole separation exceeds ∼1 nm.[39,40] In these cases, the spin−orbit interaction between the spin-singlet and triplet inter-CT states is expected to be vanishingly small, but spin conversion can still be achieved through the hyperfine interaction (HFI), which drives the periodic conversion between the singlet and the triplet spin manifolds through a dephasing in the precession of the two unpaired spins.[39,40] Indeed, mechanistic studies of D:A exciplex systems suggest a significant contribution from the HFI to the delayed emission component.[41] However, the electroluminescence external quantum efficiency (EQE_{EL}) of exciplex OLEDs generally remains low, with a record EQE_{EL} of only ∼16% reported.[38] In contrast, the EQE_{EL} for state-of-the-art TADF OLEDs reaches ∼37%.[42] This is because reducing the electron−hole overlap for a small ΔE_{ST} comes at the expense of the oscillator strength.[29] Thus, while TADF materials already have weak light absorption and emission that require careful balancing against nonradiative recombination rates,[35,43] the exciplex systems with a further increased electron−hole separation due to their inter-CT character enter a regime where the radiative emission rate starts to compare unfavorably to the nonradiative processes. Thus, OLEDs based on materials with CT-type excited states can only operate efficiently if competing nonradiative processes are strongly suppressed.

THROUGH-SPACE CHARGE TRANSFER EMITTERS

The poor OLED performance of exciplex systems is due to their low photoluminescence quantum efficiencies (Φ_{PL}),[36] indicating significant nonradiative recombination. This has been partly attributed to disorder, resulting from a lack of control over the relative orientation of the D and A materials in a thin film environment.[44] In collaboration with the group of Liang-Sheng Liao at Soochow University who designed and synthesized the studied material systems, some of the authors have recently shown that this can be overcome by exploring
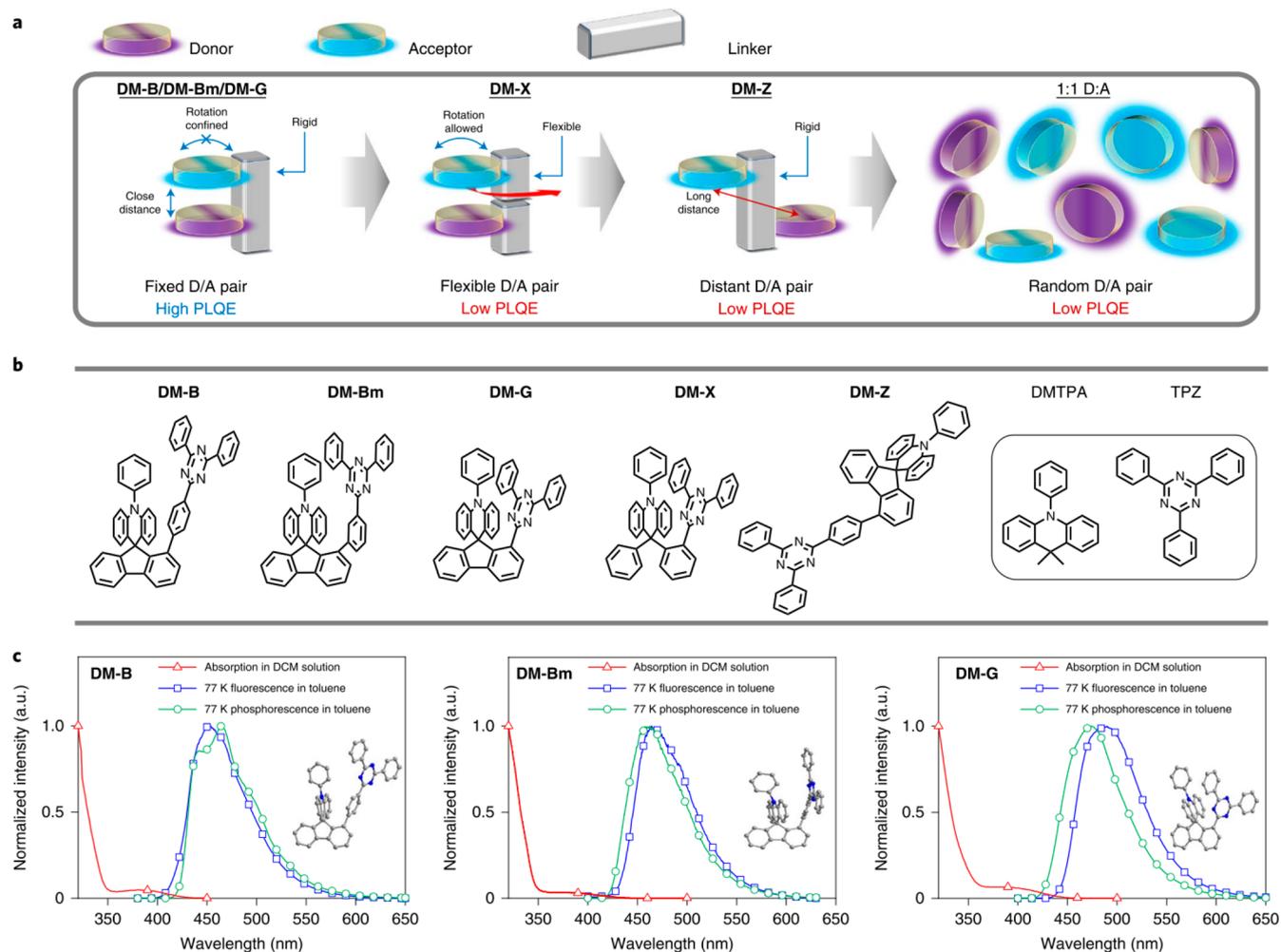
Figure 2. Through-space charge transfer emitters. (a) Illustrations of different donor:acceptor designs. (b) Chemical structures of DM-B, DM-Bm, DM-G, DM-X, and DM-Z and their molecular counterparts (DMTPA donor and TPZ acceptor). (c) Normalized absorption (room temperature, 1 × 10^{-5} M in DCM) and fluorescence and phosphorescence emission spectra (77 K, 1 × 10^{-5} M in toluene) of the rigid exciplex emitters. Insets, single-crystal X-ray structures of DM-B, DM-Bm, and DM-G. Reproduced with permission from *Nature Materials*.[44] Copyright 2020 Springer Nature.

through-space CT emitters. Here, precise control can be obtained over the exciplex-type state by employing a rigid and nonconjugated linker that fixes the D:A orientation and separation (Figure 2a,b).[44] Crucially, these novel materials differ from traditional TADF emitters as the D:A interaction is purely through space and does not involve any direct electronic conjugation. A range of systems were explored, including three model emitters synthesized using this rigid design strategy (DM-B, DM-Bm, and DM-G), two systems with increased conformational flexibility (DM-X and DM-Z), and the reference exciplex blend fabricated with a 1:1 ratio of the constituent DMTPA (9,9-dimethyl-10-phenyl-9,10-dihydroacridine) donor and TPZ (2,4,6-triphenyl-1,3,5-triazine) acceptor moieties. While excellent Φ_{PL} values of ~90% were obtained for all three rigid through-space CT emitters, with a correspondingly high EQE$_{EL}$ of 27.4% achieved for DM-B with minimal efficiency roll-off, the luminescent properties of the two flexible emitters and the reference 1:1 D:A blend were poor. This confirmed the importance of controlling the D:A orientation in exciplex-type emitters to suppress nonradiative decay, providing a novel strategy for obtaining highly efficient electroluminescence.

Beyond their excellent luminescent behavior, the through-space CT emitters exhibit several unusual properties that underpin their mechanisms of operation. For example, they show a distinctive slow prompt luminescence component, approaching hundreds of nanoseconds, characteristic of the extremely small radiative rate for the nearly pure CT state transition. However, such a slow prompt luminescence also indicates a slow forward ISC process. Despite this, the studied through-space CT emitters also demonstrate a surprisingly fast delayed luminescence component, on the order of microseconds. Indeed, rISC rates of up to ~10^{7} s^{-1} have been reported for through-space CT emitters by other groups,[45] indicating extremely rapid and efficient triplet to singlet upconversion. Assuming microscopic reversibility, the dynamics of forward and reverse ISC should be directly related,[33] meaning a slow ISC would be linked to a slow rISC process. However, this is clearly not the case in the though-space CT systems. While the lowest triplet in DM-B is a ^{3}LE state primarily located on the TPZ group, the broken conjugation of the TPZ moiety into the linker group for DM-Bm, as well as the removal of one phenyl ring from the A moiety in DM-G, renders ^{3}CT as the lowest triplet state in these compounds.
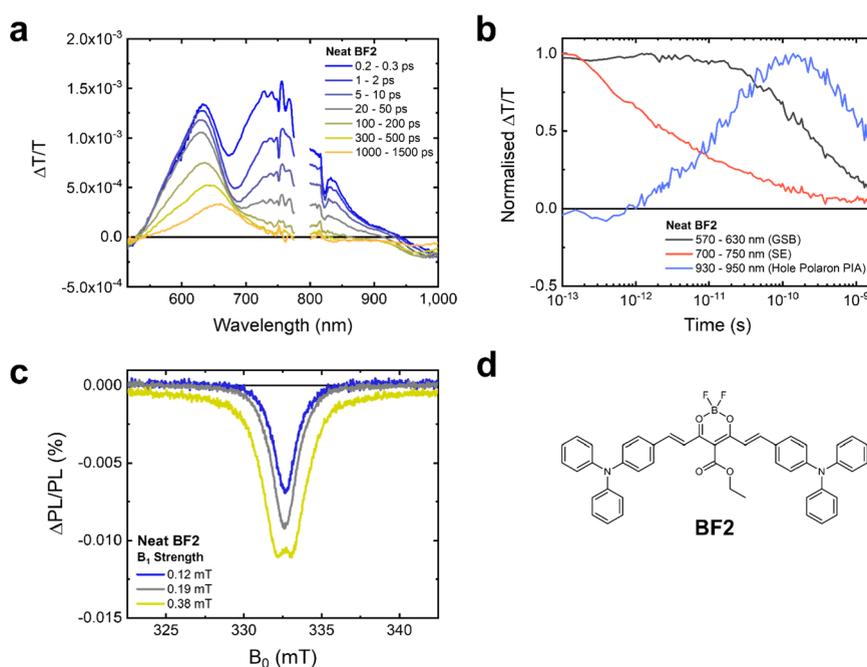
Figure 3. Spontaneous exciton dissociation in organic semiconductors. (a) Ultrafast transient absorption spectra of a neat BF2 film, excited at 610 nm with a fluence of 7.0 μJ cm^{-2}. (b) Transient absorption kinetics of the neat BF2 film, taken from the ground-state bleach (GSB; 570−630 nm), stimulated emission (SE; 700−750 nm), and hole polaron (930−950 nm) regions. (c) PLDMR response of a neat BF2 film at 293 K with 405 nm excitation (30 mW). (d) Chemical structure of BF2. Reproduced with permission from *Nature Communications*.[43] Copyright 2021 Springer Nature.

Interestingly, in the absence of a lower lying ^{3}LE, the ΔE_{ST} observed in frozen toluene solution for DM-Bm and DM-G is negative, with the ^{3}CT phosphorescence higher in energy than the low temperature ^{1}CT fluorescence (Figure 2c). One possible explanation could be the influence of the kinetic exchange energy component, which has previously been invoked to explain the possibility of a negative ΔE_{ST} between ^{1}CT and ^{3}CT in exciplex-like systems.[46] Thus, questions remain surrounding the inverted ΔE_{ST} observed in frozen solution phosphorescence measurements and what role, if any, this unusual property could be playing in the rISC process.[44] Consequently, significant combined experimental−theoretical efforts should be dedicated to understanding the optical and spin processes in this exciting new class of materials.

■ INTERCONVERTING BETWEEN INTRAMOLECULAR AND INTERMOLECULAR CHARGE TRANSFER STATES

Despite the promise shown by exciplex-type materials for effective triplet state management through the HFI, the nearly pure CT nature of the emissive singlet state means they are often severely limited by slow radiative rates and thus particularly susceptible to nonradiative recombination.[36] While careful control of the D:A orientation through a rigid linker can clearly suppress the competing nonradiative processes sufficiently for efficient OLED operation,[44] the relatively small D:A separation distances, on the order of ∼0.3 nm, mean that ΔE_{ST} will be too large for singlet−triplet interconversion driven by the HFI. Thus, balancing the competing radiative and nonradiative processes, while still maintaining access to inter-CT states beyond the nearest neighbor to benefit from the HFI contribution to rISC, presents a considerable challenge. In collaboration with the group of Frédéric Fages at Aix Marseille University who

designed and synthesized the studied compound, we have shown that these limitations can be overcome in materials that can interconvert between high-oscillator strength intramolecular excitons with large radiative rates and inter-CT states with a low exchange energy for efficient rISC mediated by the HFI.[43] This novel mechanism for OLED operation therefore combines the desirable optical attributes of conventional fluorescent emitters with the spin manipulation abilities of D:A exciplex systems.

In ref 43, a model boron difluoride curcuminoid derivative (BF2) was investigated (Figure 3), which had previously been shown to support efficient OLED operation in the near-infrared spectral region by Adachi et al.[47] Unusually for a material that was ostensibly thought to operate via a typical intramolecular TADF mechanism, BF2 possesses an extremely strong oscillator strength for its lowest energy intra-CT transition (absorption coefficient = 3.8 × 10^{5} cm^{-1}) and a relatively large ΔE_{ST} of 200 meV. This is in clear contrast to the archetypal TADF emitter 4CzIPN, which has a much weaker oscillator strength for the lowest intra-CT transition (absorption coefficient = 2.5 × 10^{4} cm^{-1}) and a smaller ΔE_{ST} of 40 meV.[43] The presence of such a strongly allowed optical transition, as well as a relatively large ΔE_{ST}, is more consistent with a traditional fluorescent emitter with significant HOMO−LUMO overlap than a typical TADF material with intra-CT character.

To explain the efficient delayed fluorescence (DF) of BF2 despite its atypical optical and electronic properties for a TADF emitter, a detailed combined experimental−theoretical study of this material was undertaken. Ultrafast transient absorption (TA) spectroscopy showed that the singlet intra-CT (intra-^{1}CT) exciton of BF2 spontaneously dissociated into inter-CT states on picosecond time scales. This can be seen through the quenching of the intense BF2 stimulated emission
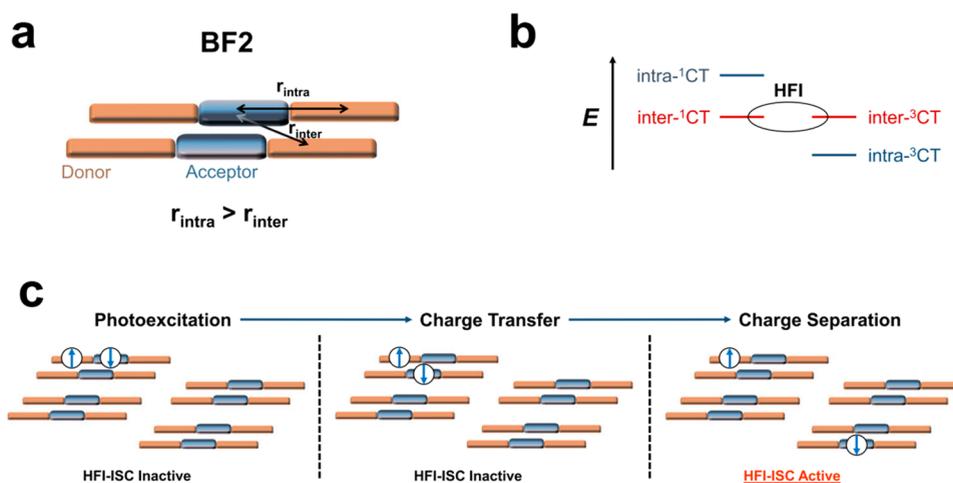
Figure 4. Role of intermolecular states in delayed fluorescence. (a) Schematic of a representative BF2 dimer demonstrating how the electron−hole separation in the inter-CT state can be less than that in the intra-CT exciton. (b) The most relevant electronic excitations (state energies not to scale) in the BF2 dimer. (c) Photophysical processes occurring in a neat BF2 film that enable efficient spin state interconversion via HFI. Reproduced with permission from *Nature Communications*.[43] Copyright 2021 Springer Nature.

(SE) feature between 700 and 850 nm and concomitant formation of the BF2 hole polaron photoinduced absorption (PIA) at 950 nm in a neat BF2 film (Figure 3a,b). Furthermore, it was discovered that spontaneous exciton dissociation could still occur efficiently in films of BF2 diluted up to 4 wt % in the noninteracting host CBP (4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl), representative of the emissive layer in OLED devices. Here, the close intermolecular interactions necessary to drive charge transfer between neighboring BF2 molecules are likely enabled by the tendency of boron difluoride curcuminoid materials to form closely interacting dimers in the solid state, even in dilute films.[48,49] TA measurements also showed the reappearance of the BF2 SE feature on nanosecond−microsecond time scales, indicating that the inter-CT states in BF2 could reform the bright molecular intra-^{1}CT exciton.

Photoluminescence-detected magnetic resonance (PLDMR) experiments confirmed the presence of inter-CT states in neat and dilute BF2 films, as evidenced by the extremely narrow full width at half-maximum (fwhm) of the resonance in Figure 3c (1.5 mT). This fwhm corresponds to an upper bound (due to line broadening effects) for the zero-field splitting (ZFS) $\mathbf{D}$ parameter of ≤ 0.75 mT (≤ 21 MHz),[50] where $\mathbf{D}$ is proportional to r^{-3} (r is the average interspin separation).[51] In contrast, $\mathbf{D}$ is typically on the order of ~ 100 mT (2800 MHz) for ^{3}LE states and ~ 20 mT (560 MHz) for triplet intra-CT (intra-^{3}CT) states in TADF materials.[33] Thus, the very small $\mathbf{D}$ for the resonance observed in BF2 indicates that the electron and hole cannot be located on the same molecule, consistent with an inter-CT state (also known as a spin-correlated radical pair[39]). Furthermore, $\mathbf{D}$ can be used to estimate the electron−hole separation in the point-charge approximation,[50] valid for systems with negligible electron−hole wave function overlap, such as inter-CT states. In BF2, $\mathbf{D} \leq 0.75$ mT corresponds to an electron−hole separation of ≥ 1.5 nm for the inter-CT state.[43] Importantly, this large electron−hole separation is in the regime where the spin exchange energy is small enough for the singlet and triplet inter-CT states to interconvert through the HFI.[52] This allows BF2 to operate in a similar way to D:A exciplex systems, but without the limitations of a very small oscillator strength for the radiative transition.

As well as estimating the electron−hole separation, PLDMR can also provide additional information about the magnitude of the HFI and the time scales of the ISC/rISC processes in the inter-CT states of BF2. This can be achieved by inducing "spin locking" in the inter-CT states,[53,54] where the magnetic field strength ($\mathbf{B}_1$) of the applied microwaves, perpendicular to the static applied field in the magnetic resonance experiment ($\mathbf{B}_0$), is increased until it overwhelms the local hyperfine field ($\mathbf{B}_{HF}$). This reduces the frequency of the HFI-induced transitions between the coupled $M_S = 0$ singlet and triplet inter-CT states and results in a characteristic "W"-shaped resonance,[53] appearing at $\mathbf{B}_1 = 0.38$ mT in BF2. The effective $\mathbf{B}_{HF}$ can then be estimated from two times the critical field strength at which the W-shaped resonance develops, giving $\mathbf{B}_{HF} \sim 0.76$ mT in BF2.[43] To gain information about the ISC/rISC time scales in the inter-CT states of BF2, $\mathbf{B}_{HF}$ can be further converted into an effective precession frequency difference between the two unpaired electron spins of 21.3 MHz, which corresponds to one complete $M_S = 0$ singlet−triplet−singlet cycle in the inter-CT state manifold. Thus, the frequency of one singlet-to-triplet conversion step is 10.65 MHz, equal to an ISC/rISC time scale of ~ 24 ns. Interestingly, we note that the singlet−triplet interconversion time of ~ 24 ns and electron−hole separation of ≥ 1.5 nm in the inter-CT states of BF2 suggest that the HFI-ISC processes observed may be in the coherent regime.[55]

To understand the spontaneous exciton dissociation process in BF2, quantum-chemical calculations were performed on representative BF2 dimers and larger aggregates, based on the crystal structure of the parent curcuminoid compound.[49] These calculations revealed that the singlet inter-CT (inter-^{1}CT) states in the BF2 dimer lie ~ 60 meV *below* the intra-^{1}CT state, implying that exciton dissociation onto the nearest molecular neighbor should be energetically favorable. This unusual energetic alignment of the molecular intra-^{1}CT exciton and inter-^{1}CT could be explained by considering the average electron−hole separation in these states. Over a range of intermolecular distances from 0.35 to 0.5 nm in the BF2 dimer, the average electron−hole separation in the inter-^{1}CT state is smaller than that in the intra-^{1}CT exciton (Figure 4a). This smaller electron−hole separation stabilizes the inter-^{1}CT
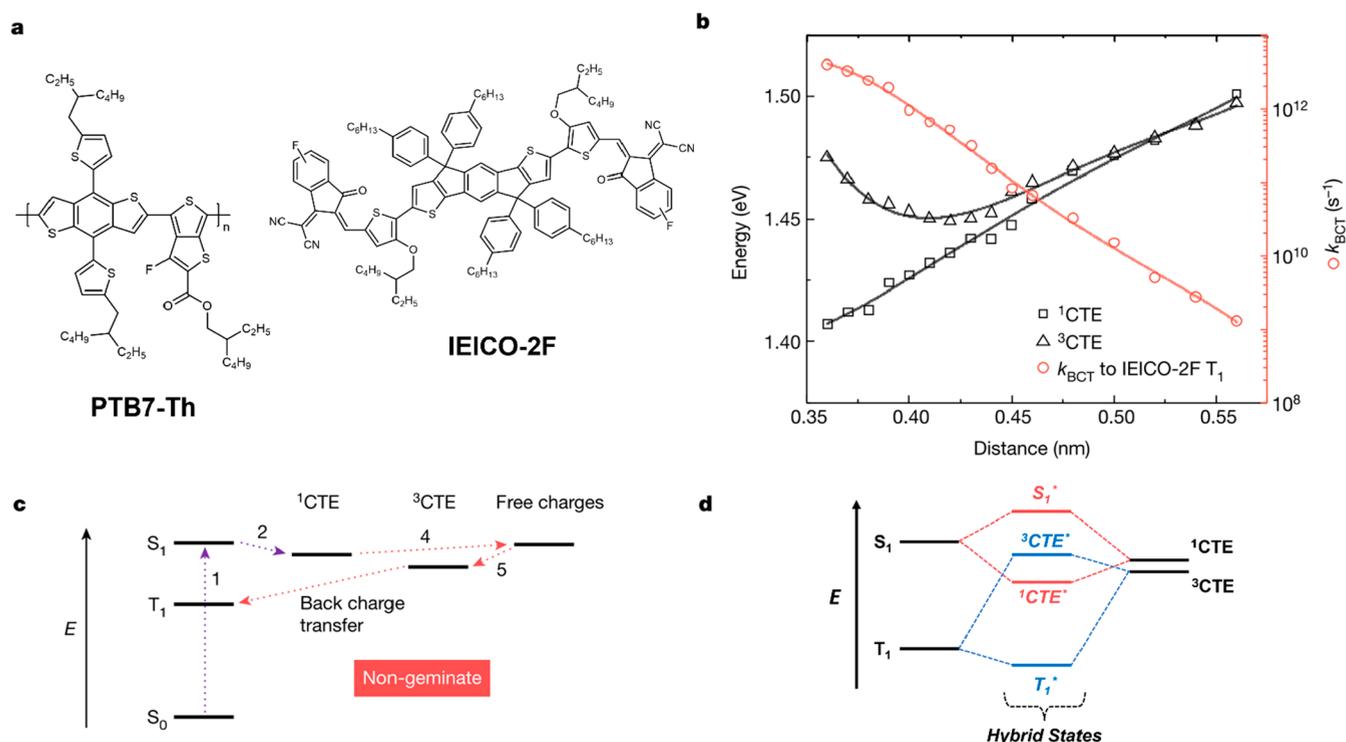
Figure 5. Role of triplet states in organic photovoltaics. (a) Diagram to illustrate the nongeminate pathway for T_1 formation in OPVs. After optical excitation (1), charge transfer from the S_1 to ^{1}CTE occurs (2). The ^{1}CTE then successfully dissociates into free charges (4). The free charges then undergo nongeminate recombination, forming a 3:1 ratio of ^{3}CTE to ^{1}CTE (5). From the ^{3}CTE, BCT to a lower energy T_1 on either the D or the A can occur. (b) Chemical structures of the donor polymer PTB7-Th and the nonfullerene acceptor IEICO-2F. (c) Results of a rigid scan of the ^{1}CTE and ^{3}CTE (equivalent to inter-^{1}CT and inter-^{3}CT states discussed in the text) energies for a representative PTB7-Th:IEICO-2F supramolecular configuration as a function of D:A separation. At each D:A separation, the rate of back charge transfer, k_{BCT}, from ^{3}CTE to T_1 of the NFA has also been calculated. The solid lines provide polynomial guides to the eye. (d) Schematic to represent the effect of hybridization between the molecular excitons and charge transfer excitons on the energetic ordering of the ^{1}CTE and ^{3}CTE. Reproduced with permission from *Nature*.[9] Copyright 2021 Springer Nature.

state relative to the intra-^{1}CT exciton, providing a driving force for charge transfer between neighboring BF2 molecules (Figure 4b). Further calculations on a BF2 tetramer suggested that the second nearest neighbor inter-^{1}CT states, with an average electron−hole separation of ∼1 nm, were also in close energy resonance with the intra-^{1}CT exciton. Thus, the electronic excitations of BF2 will be able to freely explore the excited-state manifolds with electron−hole separations up to ∼1 nm, allowing facile interconversion between intra-molecular and intermolecular states. In addition, it is expected that electron−hole separations beyond 1 nm in the inter-CT manifold will be thermally accessible, allowing longer range charge separation. Through calculations on the hyperfine couplings in the BF2 dimer, it was confirmed that ΔE_{ST} between the inter-^{1}CT and the triplet inter-CT (inter-^{3}CT) became small enough to enable HFI-ISC processes approaching the rate determined from the PLDMR measurements (∼10^7 s^{-1}) at electron−hole separations ≥ 1 nm, supporting the experimental observations.

The combined experimental−theoretical work on BF2 informed the development of a novel mechanism of OLED operation involving inter-CT states (Figure 4c). Upon the injection of electrons and holes, inter-CT states are generated in a spin-statistical manner when the free electrons and holes initially come within their Coulomb capture radius. The 25% inter-^{1}CT states created act as a reservoir for the formation of the bright intra-^{1}CT exciton with an extremely high radiative

rate. The 75% of injected carriers that form inter-^{3}CT states are expected to branch among (i) conversion into inter-^{1}CT via HFI-ISC; (ii) dissociation into free charge carriers that are then recycled in the recombination loop; and (iii) recombination into lower-lying intra-^{3}CT excitons. Importantly, pathway (iii) does not represent a terminal loss event as BF2 possesses a (slow) intramolecular rISC pathway.[43]

■ THE ROLE OF TRIPLET STATES IN ORGANIC PHOTOVOLTAICS

It is well-known that the primary cause of the low V_{OC} in OPVs is excessive nonradiative recombination,[56] which impacts the V_{OC} of the solar cell by reducing the charge carrier lifetime from the intrinsic radiative limit.[13−15] This nonradiative voltage loss (ΔV_{nr}) can be directly calculated from the EQE_{EL} of the solar cell run at moderate forward bias as a light-emitting diode:

$$\Delta V_{nr} = \frac{-k_B T}{q} \ln(EQE_{EL}) \tag{1}$$

where k_B is the Boltzmann constant and T is the temperature. Here, the EQE_{EL} can be further separated into the different contributions:[8]

$$EQE_{EL} = \gamma \Phi_{PL} \chi \eta_{out} \tag{2}$$

where γ is the charge balance factor, χ is the fraction of recombination events that can decay radiatively (spin-singlet
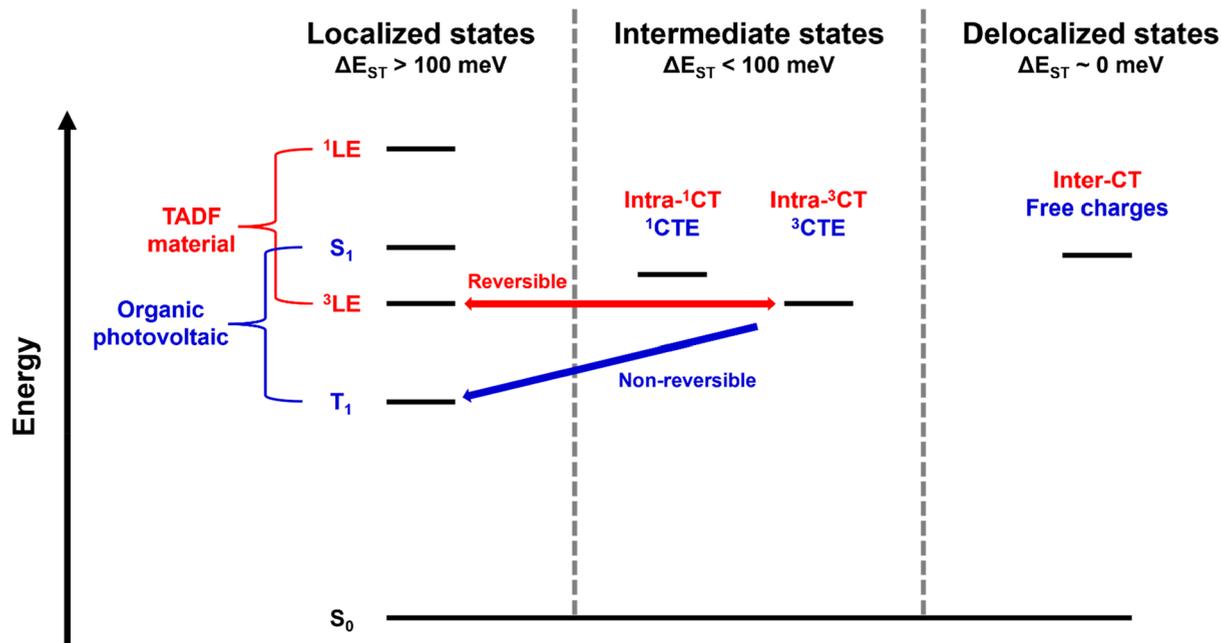
Figure 6. Jablonski diagram showing the equivalence between the electronic excitations of a TADF material and an organic photovoltaic. The excited states labeled in red are those relevant to a TADF material, while the states labeled in blue are those relevant to an organic photovoltaic.

excitations), and η_{out} is the photon out-coupling efficiency. In state-of-the-art NFA OPVs, ΔV_{nr} is ~200 mV.[57] This contrasts with inorganic technologies, where ΔV_{nr} can reach <100 mV.[58,59] To address this deficit, the field has recently been focused on improving Φ_{PL} of the low band gap component in a neat film, which is considered to provide the upper bound for Φ_{PL} in a low-offset blend where recombination can proceed via the lowest energy S_1 state in the system.[60,61] In contrast to OLEDs, it had been noted that triplet management was a relatively understudied topic in OPVs.[12,17,62−64] However, there have now been several recent reports on the critical role of recombination via T_1 in NFA OPVs.[9−12] As with OLEDs, it is generally expected that the T_1 state on the low band gap component will be the lowest energy excitation in the OPV system and could act as a trap state for nonradiative recombination.[9] Indeed, the nongeminate recombination of free charge carriers in an OPV is also expected to produce, to a first approximation, 25% spin-singlet and 75% spin-triplet states following spin statistics.[19] Thus, it is conceivable that triplet recombination could be a significant loss mechanism in OPVs. This was recently confirmed when it was shown that about 90% of free charge recombination proceeded via the Y6 T_1 state in the benchmark PM6:Y6 blend.[9] As a result, χ is limited to 0.1, and the EQE_{EL} of the OPV is reduced by a factor of 10, corresponding to ~60 mV of additional ΔV_{nr}. It has been demonstrated that to obtain a reduction in ΔV_{nr} equivalent to that from removing recombination via T_1, the Φ_{PL} of Y6 (in a neat film) would need to rise from 2% to ~20%;[17] this would be an unprecedented value among fluorescent organic small molecules with an emission peak around 950 nm[65] and, moreover, in a molecule that can also operate as an electron acceptor in a highly efficient OPV. Thus, if the step-change in V_{OC} required for PCEs > 20% is to be realized, effective triplet management strategies, which have long been recognized as essential for the efficient operation of OLEDs, must be developed in OPVs.

CHARGE TRANSFER STATES CONTROL TRIPLET RECOMBINATION IN ORGANIC PHOTOVOLTAICS

In OPVs, the nongeminate recombination of free charge carriers proceeds via the formation of inter-CT states where an electron is located on the A component and a hole is located on the D material (Figure 5a), with ~75% of these events initially forming triplet charge transfer excitons (^{3}CTEs) and 25% singlet charge transfer excitons (^{1}CTEs),[19] where these CTEs can be considered electronically equivalent to the inter-CT states previously discussed in the context of OLEDs. Thus, the ^{3}CTE state acts as a critical intermediate in the T_1 formation process. Indeed, this situation is comparable to that reported in BF2, where redissociation of the inter-^{3}CT into free charges, conversion into inter-^{1}CT states via HFI-ISC, and back charge transfer into T_1 are all possible outcomes.[43] However, in the case of NFA OPVs, the rate of the back charge transfer process from ^{3}CTE to T_1 at the D:A interface can be extremely fast: up to ~10^{12} s^{-1}, as confirmed by experiment and calculations.[9] In addition, by tracking the growth of the electro-absorption feature of the polymer,[66] it was shown that the dissociation rate of thermalized CTE states located at the D:A interface was on the order of $10^{10}-10^{11}$ s^{-1} in the studied NFA blends.[9] However, HFI-ISC from ^{3}CTE to ^{1}CTE, with a rate on the order of ~10^7 s^{-1}, is too slow to compete.[43,52] Therefore, the critical competition that controls T_1 formation in OPVs is between the rates of back charge transfer and redissociation of inter-^{3}CT, with back charge transfer often dominating.

One promising tactic for effective triplet state management in OPVs involves manipulating the exchange energy of the critical CTE states.[9] This can be achieved by designing systems with (i) close energy resonance between the CTE and molecular exciton states; (ii) strong overlap and phase matching of the frontier molecular orbital (FMO) wave functions of the D and A components; and (iii) spatial registry between the D and A materials, to allow for the close intermolecular contacts necessary for strong wave function

interactions. If these conditions are fulfilled, it is possible to induce significant hybridization between the CTE and the molecular exciton states,[60,61,67,68] which results in an unusual negative ΔE_{ST} and thus energetic inversion of the ^{1}CTE and ^{3}CTE states. This was shown in a model system developed by the groups of Thuc-Quyen Nguyen and Guillermo C. Bazan at the University of California at Santa Barbara, consisting of the polymer PTB7-Th blended with the NFA IEICO-2F (Figure 5b),[69] which did not experimentally show T_1 formation following the recombination of free charges. By exploring the distance dependence of the ^{1}CTE and ^{3}CTE state energies, hybridization effects, which are stronger at closer distances where the electronic coupling is larger, result in the energetic minima of the ^{3}CTE state being shifted back from the D:A interface (Figure 5c,d). Practically, this means that it is energetically unfavorable for the electron−hole pair in the ^{3}CTE spin configuration to approach the D:A interface. As the calculated back charge transfer rate from the ^{3}CTE to T_1 of the NFA rapidly falls with distance, the important consequence is that the rate of this process can be reduced by at least an order of magnitude by hybridization effects. This results in the back charge transfer rate becoming comparable to, or indeed slower than, the rate of CTE state dissociation in NFA OPVs, meaning that recombination into T_1 can be suppressed. Through exploring several model OPV systems, provided by Feng Gao at Linköping University and the groups at the University of California at Santa Barbara, excellent agreement between experiment and theory was found, with only D:A combinations that possessed significant hybridization showing suppressed recombination into T_1.[9] Indeed, despite possessing a very low Φ_{PL} of 0.6% for a neat film of the NFA component, PTB7-Th:IEICO-0F, which is closely related to PTB7-Th:IEICO-2F discussed above, exhibited the lowest ΔV_{nr} in the study, which was directly attributed to the suppressed nonradiative T_1 losses in this blend. Thus, hybridization of the ^{3}CTE and T_1 electronic states presents an important advance for triplet management in NFA OPVs, which is expected to reduce ΔV_{nr} and push PCEs toward the important 20% milestone.

◼ THE EQUIVALENCE BETWEEN OLEDs AND ORGANIC PHOTOVOLTAICS

Though our discussions have thus far treated OLEDs and OPVs separately, we consider there to be an important equivalence between these two closely related systems. We show in Figure 6 a Jablonski-type diagram of the critical electronic states involved in a TADF material (red) and an OPV (blue) to indicate how the description of both systems are interchangeable. On the left, we include the localized states: for a TADF, these are the singlet local exciton (^{1}LE) and ^{3}LE on the D or A moieties; in an OPV, these are the molecular S_1 and T_1 excitons. Due to their highly localized nature, there is a significant exchange energy ($\Delta E_{ST} > 100$ meV), and rISC is not possible. In the middle are the intermediate states with some CT character and a reduced exchange energy ($\Delta E_{ST} < 100$ meV): in a TADF, these are the intra-^{1}CT and intra-^{3}CT; in OPVs, this is the interfacial ^{1}CTE and ^{3}CTE formed between the D and the A materials (which we reiterate can be considered electronically equivalent to inter-^{1}CT and inter-^{3}CT located on neighboring molecules in exciplex OLED systems). In this intermediary manifold, rISC can proceed relatively efficiently in the presence of sufficient

spin−orbit coupling, assisted by ambient thermal energy. Finally, on the right are the delocalized states, in which the exchange interaction is vanishingly small ($\Delta E_{ST} \sim 0$ meV). These are the inter-CT states for both OLEDs and OPVs in which the electron and hole have achieved longer range charge separation (>1 nm), like those in BF2,[43] or even free charge carriers. In these well-separated electronic excitations, rISC is facile, owing to the HFI which can rapidly interconvert the singlet and triplet manifolds on time scales of tens of nanoseconds.[43,52] Furthermore, scrambling of the spin states by consecutive cycles of interconversion between inter-CT states and spin uncorrelated free charge carriers can also provide an efficient pathway to achieve singlet−triplet interconversion. However, the key difference between a TADF material and an OPV is the alignment of the localized and intermediate states: the localized states are significantly downshifted in energy relative to the intermediate states in an OPV. Thus, current OPV designs can be thought of as an inefficient TADF system, where the nonoptimal alignment of the ^{3}LE (T_1) with the intra-^{3}CT (^{3}CTE) allows for the trapping of excitations in the ^{3}LE (T_1) state. Following this, the nonradiative triplet recombination processes observed in an OPV, such as triplet-charge annihilation,[9] can proceed unabated.

For an OPV to efficiently recycle T_1 states formed via nongeminate recombination, the energetic offset between T_1 and ^{3}CTE should be reduced to mirror more closely that of a well-designed TADF material. However, simply upshifting the S_1 and T_1 is not a viable tactic, as it will simultaneously increase the energy gap between S_1 and ^{1}CTE, increasing the voltage losses associated with a large S_1-^{1}CTE offset.[60,61,70] Instead, we believe that the field needs to design low band gap NFA materials with a reduced exchange energy and a consequently smaller ΔE_{ST}. However, the key challenge to overcome is that a smaller exchange energy is nominally associated with weaker light absorption, which is not ideal for solar cell applications. Thus, simply creating NFA materials that possess excited states with increased intra-CT character may not necessarily be the most effective tactic in terms of simultaneously achieving high PCEs. Instead, more advanced strategies should be investigated, such as designing materials with short-range charge transfer that reduces ΔE_{ST} while maintaining the oscillator strength[34,35] or encouraging the selective delocalization of the S_1 wave function over neighboring molecules to lower the S_1 state energy without impacting T_1, thus reducing ΔE_{ST}.[71] Indeed, strong intermolecular interactions and significantly red-shifted absorptions in neat films compared to dilute solutions, indicative of S_1 stabilization, have already been reported for the high-performance NFA material Y6 and its derivatives,[72−74] indicating a potential set of existing and well-studied materials that can act as a platform for further optimization.

◼ DISCUSSION AND CONCLUSIONS

As we have discussed, triplet management in organic semiconductors is a critical topic for the development of highly efficient optoelectronic devices. Indeed, efforts in this broad area are driving significant innovations in both material design and spin manipulation tactics. This work is particularly advanced in the field of OLEDs, where active research efforts on systems that can take advantage of excited states with CT character and reduced exchange energies are at the forefront of providing rapid and efficient mechanisms for interconversion

between the singlet and the triplet spin manifolds. In particular, the successful control and utilization of the HFI to drive spin state interconversion in inter-CT states represents a significant breakthrough that should be further refined and exploited.

Though previously overlooked, triplet management is now coming to the forefront of research efforts in OPVs, driven by the desire to finally realize the long-standing potential of this promising next-generation technology. However, while some success has been achieved by manipulating the energetics and kinetics of the ^{3}CTE states through hybridization effects, more efforts are needed on this important topic. To this end, we believe that the OPV field should seek inspiration from OLEDs, where triplet management strategies have already been extensively developed. Indeed, as it is well-known that a good solar cell should also be an excellent LED, the optimization of OPVs as an OLED is the natural next step to take.[75] In particular, the development of NFAs with a reduced ΔE_{ST} to allow for the recycling of any T_1 states formed, inspired by TADFs, represents a promising strategy that should be considered.

■ AUTHOR INFORMATION

Corresponding Authors

Alexander J. Gillett − *Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom;* ⓘ orcid.org/0000-0001-7572-7333; Email: ajg216@cam.ac.uk

David Beljonne − *Laboratory for Chemistry of Novel Materials, Université de Mons, 7000 Mons, Belgium;* ⓘ orcid.org/0000-0002-2989-3557; Email: david.beljonne@umons.ac.be

Author

Richard H. Friend − *Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom;* ⓘ orcid.org/0000-0001-6565-6308

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.chemmater.2c01301

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Biographies

Alexander J. Gillett received his Ph.D. in Physics from the University of Cambridge under the supervision of Prof. Sir Richard Friend, where he is currently a Research Associate in the Optoelectronics group. Before joining the University of Cambridge, he worked as a researcher on organic solar cells at Merck KGaA. His current research focuses on novel spin management strategies in organic semiconductor materials and devices.

Professor Richard H. Friend is in the Department of Physics at the University of Cambridge. His research encompasses the physics, materials science, and engineering of semiconductor devices made with carbon-based semiconductors, particularly polymers.

David Beljonne is a research director of the Belgian National Science Foundation (FNRS) at the University of Mons. His research activities deal with a multifaceted modelling of the optoelectronic processes taking place in the bulk and at interfaces of (semi)conducting organic, 2D, and hybrid materials for optoelectronics and energy applications.

■ ABBREVIATIONS

OLED, organic light emitting diode; OPV, organic photovoltaic; PCE, power conversion efficiency; NFA, nonfullerene acceptor; FA, fullerene acceptor; TADF, thermally activated delayed fluorescence; rISC, reverse intersystem crossing; PLDMR, photoluminescence-detected magnetic resonance; HFI, hyperfine interaction; HOMO, highest-occupied molecular orbital; LUMO, lowest-unoccupied molecular orbital; FMO, frontier molecular orbital

■ REFERENCES

(1) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly Efficient Organic Light-Emitting Diodes from Delayed Fluorescence. *Nature* **2012**, *492* (7428), 234−238.

(2) Zheng, Z.; Wang, J.; Bi, P.; Ren, J.; Wang, Y.; Yang, Y.; Liu, X.; Zhang, S.; Hou, J. Tandem Organic Solar Cell with 20.2% Efficiency. *Joule* **2022**, *6* (1), 171−184.

(3) Bi, P.; Zhang, S.; Chen, Z.; Xu, Y.; Cui, Y.; Zhang, T.; Ren, J.; Qin, J.; Hong, L.; Hao, X.; Hou, J. Reduced Non-Radiative Charge Recombination Enables Organic Photovoltaic Cell Approaching 19% Efficiency. *Joule* **2021**, *5* (9), 2408−2419.

(4) Cui, Y.; Xu, Y.; Yao, H.; Bi, P.; Hong, L.; Zhang, J.; Zu, Y.; Zhang, T.; Qin, J.; Ren, J.; Chen, Z.; He, C.; Hao, X.; Wei, Z.; Hou, J. Single-Junction Organic Photovoltaic Cell with 19% Efficiency. *Adv. Mater.* **2021**, *33* (41), 2102420.

(5) Clarke, T. M.; Durrant, J. R. Charge Photogeneration in Organic Solar Cells. *Chem. Rev.* **2010**, *110* (11), 6736−6767.

(6) Köhler, A.; Beljonne, D. The Singlet−Triplet Exchange Energy in Conjugated Polymers. *Adv. Funct. Mater.* **2004**, *14* (1), 11−18.

(7) Hirata, S. Recent Advances in Materials with Room-Temperature Phosphorescence: Photophysics for Triplet Exciton Stabilization. *Adv. Opt. Mater.* **2017**, *5* (17), 1700116.

(8) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. Electroluminescence in Conjugated Polymers. *Nature* **1999**, *397* (6715), 121−128.

(9) Gillett, A. J.; Privitera, A.; Dilmurat, R.; Karki, A.; Qian, D.; Pershin, A.; Londi, G.; Myers, W. K.; Lee, J.; Yuan, J.; Ko, S.-J.; Riede, M. K.; Gao, F.; Bazan, G. C.; Rao, A.; Nguyen, T.-Q.; Beljonne, D.; Friend, R. H. The Role of Charge Recombination to Triplet Excitons in Organic Solar Cells. *Nature* **2021**, *597* (7878), 666−671.

(10) Wang, R.; Xu, J.; Fu, L.; Zhang, C.; Li, Q.; Yao, J.; Li, X.; Sun, C.; Zhang, Z.-G.; Wang, X.; Li, Y.; Ma, J.; Xiao, M. Nonradiative Triplet Loss Suppressed in Organic Photovoltaic Blends with Fluoridated Nonfullerene Acceptors. *J. Am. Chem. Soc.* **2021**, *143* (11), 4359−4366.

(11) Chen, Z.; Chen, X.; Jia, Z.; Zhou, G.; Xu, J.; Wu, Y.; Xia, X.; Li, X.; Zhang, X.; Deng, C.; Zhang, Y.; Lu, X.; Liu, W.; Zhang, C.; Yang, Y.; Zhu, H. Triplet Exciton Formation for Non-Radiative Voltage Loss in High-Efficiency Nonfullerene Organic Solar Cells. *Joule* **2021**, *5* (7), 1832−1844.

(12) Marin-Beloqui, J. M.; Toolan, D. T. W.; Panjwani, N. A.; Limbu, S.; Kim, J.; Clarke, T. M. Triplet-Charge Annihilation in a Small Molecule Donor: Acceptor Blend as a Major Loss Mechanism in Organic Photovoltaics. *Adv. Energy Mater.* **2021**, *11* (24), 2100539.

(13) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of P-n Junction Solar Cells. *J. Appl. Phys.* **1961**, *32* (3), 510−519.

(14) Ross, R. T. Some Thermodynamics of Photochemical Systems. *J. Chem. Phys.* **1967**, *46* (12), 4590−4593.

(15) Rau, U. Reciprocity Relation between Photovoltaic Quantum Efficiency and Electroluminescent Emission of Solar Cells. *Phys. Rev. B* **2007**, *76* (8), No. 085303.

(16) Liu, Y.; Zhao, J.; Li, Z.; Mu, C.; Ma, W.; Hu, H.; Jiang, K.; Lin, H.; Ade, H.; Yan, H. Aggregation and Morphology Control Enables Multiple Cases of High-Efficiency Polymer Solar Cells. *Nat. Commun.* **2014**, *5* (1), 5293.

(17) Privitera, A.; Grüne, J.; Karki, A.; Myers, W. K.; Dyakonov, V.; Nguyen, T.; Riede, M. K.; Friend, R. H.; Sperlich, A.; Gillett, A. J. Geminate and Nongeminate Pathways for Triplet Exciton Formation in Organic Solar Cells. *Adv. Energy Mater.* **2022**, *12*, 2103944.

(18) Chow, P. C. Y.; Gélinas, S.; Rao, A.; Friend, R. H. Quantitative Bimolecular Recombination in Organic Photovoltaics through Triplet Exciton Formation. *J. Am. Chem. Soc.* **2014**, *136* (9), 3424−3429.

(19) Rao, A.; Chow, P. C. Y.; Gélinas, S.; Schlenker, C. W.; Li, C.-Z.; Yip, H.-L.; Jen, A. K.-Y.; Ginger, D. S.; Friend, R. H. The Role of Spin in the Kinetic Control of Recombination in Organic Photovoltaics. *Nature* **2013**, *500* (7463), 435−439.

(20) Di Nuzzo, D.; Aguirre, A.; Shahid, M.; Gevaerts, V. S.; Meskers, S. C. J.; Janssen, R. A. J. Improved Film Morphology Reduces Charge Carrier Recombination into the Triplet Excited State in a Small Bandgap Polymer-Fullerene Photovoltaic Cell. *Adv. Mater.* **2010**, *22* (38), 4321−4324.

(21) Menke, S. M.; Sadhanala, A.; Nikolka, M.; Ran, N. A.; Ravva, M. K.; Abdel-Azeim, S.; Stern, H. L.; Wang, M.; Sirringhaus, H.; Nguyen, T.-Q.; Brédas, J.-L.; Bazan, G. C.; Friend, R. H. Limits for Recombination in a Low Energy Loss Organic Heterojunction. *ACS Nano* **2016**, *10* (12), 10736−10744.

(22) Karuthedath, S.; Gorenflot, J.; Melianas, A.; Kan, Z.; Kemerink, M.; Laquai, F. Buildup of Triplet-State Population in Operating TQ1:PC71BM Devices Does Not Limit Their Performance. *J. Phys. Chem. Lett.* **2020**, *11* (8), 2838−2845.

(23) Benduhn, J.; Piersimoni, F.; Londi, G.; Kirch, A.; Widmer, J.; Koerner, C.; Beljonne, D.; Neher, D.; Spoltore, D.; Vandewal, K. Impact of Triplet Excited States on the Open-Circuit Voltage of Organic Solar Cells. *Adv. Energy Mater.* **2018**, *8* (21), 1800451.

(24) Dimitrov, S. D.; Wheeler, S.; Niedzialek, D.; Schroeder, B. C.; Utzat, H.; Frost, J. M.; Yao, J.; Gillett, A.; Tuladhar, P. S.; McCulloch, I.; Nelson, J.; Durrant, J. R. Polaron Pair Mediated Triplet Generation in Polymer/Fullerene Blends. *Nat. Commun.* **2015**, *6* (1), 6501.

(25) Salvadori, E.; Luke, N.; Shaikh, J.; Leventis, A.; Bronstein, H.; Kay, C. W. M.; Clarke, T. M. Ultra-Fast Spin-Mixing in a Diketopyrrolopyrrole Monomer/Fullerene Blend Charge Transfer State. *J. Mater. Chem. A* **2017**, *5* (46), 24335−24343.

(26) Cui, L.-S.; Gillett, A. J.; Zhang, S.-F.; Ye, H.; Liu, Y.; Chen, X.-K.; Lin, Z.-S.; Evans, E. W.; Myers, W. K.; Ronson, T. K.; Nakanotani, H.; Reineke, S.; Bredas, J.-L.; Adachi, C.; Friend, R. H. Fast Spin-Flip Enables Efficient and Stable Organic Electroluminescence from Charge-Transfer States. *Nat. Photonics* **2020**, *14* (10), 636−642.

(27) Czerwieniec, R.; Yu, J.; Yersin, H. Blue-Light Emission of Cu(I) Complexes and Singlet Harvesting. *Inorg. Chem.* **2011**, *50* (17), 8293−8301.

(28) Kaji, H.; Suzuki, H.; Fukushima, T.; Shizu, K.; Suzuki, K.; Kubo, S.; Komino, T.; Oiwa, H.; Suzuki, F.; Wakamiya, A.; Murata, Y.; Adachi, C. Purely Organic Electroluminescent Material Realizing 100% Conversion from Electricity to Light. *Nat. Commun.* **2015**, *6* (1), 8476.

(29) Endo, A.; Ogasawara, M.; Takahashi, A.; Yokoyama, D.; Kato, Y.; Adachi, C. Thermally Activated Delayed Fluorescence from Sn4+-Porphyrin Complexes and Their Application to Organic Light Emitting Diodes - A Novel Mechanism for Electroluminescence. *Adv. Mater.* **2009**, *21* (47), 4802−4806.

(30) Etherington, M. K.; Gibson, J.; Higginbotham, H. F.; Penfold, T. J.; Monkman, A. P. Revealing the Spin−Vibronic Coupling Mechanism of Thermally Activated Delayed Fluorescence. *Nat. Commun.* **2016**, *7* (1), 13680.

(31) Gibson, J.; Monkman, A. P.; Penfold, T. J. The Importance of Vibronic Coupling for Efficient Reverse Intersystem Crossing in Thermally Activated Delayed Fluorescence Molecules. *ChemPhysChem* **2016**, *17* (19), 2956−2961.

(32) Noda, H.; Chen, X.-K.; Nakanotani, H.; Hosokai, T.; Miyajima, M.; Notsuka, N.; Kashima, Y.; Brédas, J.-L.; Adachi, C. Critical Role of Intermediate Electronic States for Spin-Flip Processes in Charge-Transfer-Type Organic Molecules with Multiple Donors and Acceptors. *Nat. Mater.* **2019**, *18* (10), 1084−1090.

(33) Drummond, B. H.; Aizawa, N.; Zhang, Y.; Myers, W. K.; Xiong, Y.; Cooper, M. W.; Barlow, S.; Gu, Q.; Weiss, L. R.; Gillett, A. J.; Credgington, D.; Pu, Y.-J.; Marder, S. R.; Evans, E. W. Electron Spin Resonance Resolves Intermediate Triplet States in Delayed Fluorescence. *Nat. Commun.* **2021**, *12* (1), 4532.

(34) Hatakeyama, T.; Shiren, K.; Nakajima, K.; Nomura, S.; Nakatsuka, S.; Kinoshita, K.; Ni, J.; Ono, Y.; Ikuta, T. Ultrapure Blue Thermally Activated Delayed Fluorescence Molecules: Efficient HOMO-LUMO Separation by the Multiple Resonance Effect. *Adv. Mater.* **2016**, *28* (14), 2777−2781.

(35) Pershin, A.; Hall, D.; Lemaur, V.; Sancho-Garcia, J.-C.; Muccioli, L.; Zysman-Colman, E.; Beljonne, D.; Olivier, Y. Highly Emissive Excitons with Reduced Exchange Energy in Thermally Activated Delayed Fluorescent Molecules. *Nat. Commun.* **2019**, *10* (1), 597.

(36) Goushi, K.; Yoshida, K.; Sato, K.; Adachi, C. Organic Light-Emitting Diodes Employing Efficient Reverse Intersystem Crossing for Triplet-to-Singlet State Conversion. *Nat. Photonics* **2012**, *6* (4), 253−258.

(37) Sarma, M.; Wong, K.-T. Exciplex: An Intermolecular Charge-Transfer Approach for TADF. *ACS Appl. Mater. Interfaces* **2018**, *10* (23), 19279−19304.

(38) Lin, T.-C.; Sarma, M.; Chen, Y.-T.; Liu, S.-H.; Lin, K.-T.; Chiang, P.-Y.; Chuang, W.-T.; Liu, Y.-C.; Hsu, H.-F.; Hung, W.-Y.; Tang, W.-C.; Wong, K.-T.; Chou, P.-T. Probe Exciplex Structure of Highly Efficient Thermally Activated Delayed Fluorescence Organic Light Emitting Diodes. *Nat. Commun.* **2018**, *9* (1), 3111.

(39) Steiner, U. E.; Ulrich, T. Magnetic Field Effects in Chemical Kinetics and Related Phenomena. *Chem. Rev.* **1989**, *89* (1), 51−147.

(40) McLauchlan, K. A.; Steiner, U. E. The Spin-Correlated Radical Pair as a Reaction Intermediate. *Mol. Phys.* **1991**, *73* (2), 241−263.

(41) Hontz, E.; Chang, W.; Congreve, D. N.; Bulović, V.; Baldo, M. A.; Van Voorhis, T. The Role of Electron−Hole Separation in Thermally Activated Delayed Fluorescence in Donor−Acceptor Blends. *J. Phys. Chem. C* **2015**, *119* (45), 25591−25597.

(42) Lin, T.-A.; Chatterjee, T.; Tsai, W.-L.; Lee, W.-K.; Wu, M.-J.; Jiao, M.; Pan, K.-C.; Yi, C.-L.; Chung, C.-L.; Wong, K.-T.; Wu, C.-C. Sky-Blue Organic Light Emitting Diode with 37% External Quantum Efficiency Using Thermally Activated Delayed Fluorescence from Spiroacridine-Triazine Hybrid. *Adv. Mater.* **2016**, *28* (32), 6976−6983.

(43) Gillett, A. J.; Tonnelé, C.; Londi, G.; Ricci, G.; Catherin, M.; Unson, D. M. L.; Casanova, D.; Castet, F.; Olivier, Y.; Chen, W. M.; Zaborova, E.; Evans, E. W.; Drummond, B. H.; Conaghan, P. J.; Cui, L.-S.; Greenham, N. C.; Puttisong, Y.; Fages, F.; Beljonne, D.; Friend, R. H. Spontaneous Exciton Dissociation Enables Spin State Interconversion in Delayed Fluorescence Organic Semiconductors. *Nat. Commun.* **2021**, *12* (1), 6640.

(44) Tang, X.; Cui, L.-S.; Li, H.-C.; Gillett, A. J.; Auras, F.; Qu, Y.-K.; Zhong, C.; Jones, S. T. E.; Jiang, Z.-Q.; Friend, R. H.; Liao, L.-S. Highly Efficient Luminescence from Space-Confined Charge-Transfer Emitters. *Nat. Mater.* **2020**, *19* (12), 1332−1338.

(45) Wada, Y.; Nakagawa, H.; Matsumoto, S.; Wakisaka, Y.; Kaji, H. Organic Light Emitters Exhibiting Very Fast Reverse Intersystem Crossing. *Nat. Photonics* **2020**, *14* (10), 643−649.

(46) Difley, S.; Beljonne, D.; Van Voorhis, T. On the Singlet−Triplet Splitting of Geminate Electron−Hole Pairs in Organic Semiconductors. *J. Am. Chem. Soc.* **2008**, *130* (11), 3420−3427.

(47) Kim, D.-H.; D'Aléo, A.; Chen, X.-K.; Sandanayaka, A. D. S.; Yao, D.; Zhao, L.; Komino, T.; Zaborova, E.; Canard, G.; Tsuchiya, Y.; Choi, E.; Wu, J. W.; Fages, F.; Brédas, J.-L.; Ribierre, J.-C.; Adachi, C. High-Efficiency Electroluminescence and Amplified Spontaneous Emission from a Thermally Activated Delayed Fluorescent near-Infrared Emitter. *Nat. Photonics* **2018**, *12* (2), 98−104.

(48) Felouat, A.; D'Aléo, A.; Fages, F. Synthesis and Photophysical Properties of Difluoroboron Complexes of Curcuminoid Derivatives Bearing Different Terminal Aromatic Units and a Meso -Aryl Ring. *J. Org. Chem.* **2013**, *78* (9), 4446−4455.

(49) Archet, F.; Yao, D.; Chambon, S.; Abbas, M.; D'Aléo, A.; Canard, G.; Ponce-Vargas, M.; Zaborova, E.; Le Guennic, B.; Wantz, G.; Fages, F. Synthesis of Bioinspired Curcuminoid Small Molecules for Solution-Processed Organic Solar Cells with High Open-Circuit Voltage. *ACS Energy Lett.* **2017**, *2* (6), 1303−1307.

(50) Bunzmann, N.; Krugmann, B.; Weissenseel, S.; Kudriashova, L.; Ivaniuk, K.; Stakhira, P.; Cherpak, V.; Chapran, M.; Grybauskaite-Kaminskiene, G.; Grazulevicius, J. V.; Dyakonov, V.; Sperlich, A. Spin- and Voltage-Dependent Emission from Intra- and Intermolecular TADF OLEDs. *Adv. Electron. Mater.* **2021**, *7* (3), 2000702.

(51) Richert, S.; Tait, C. E.; Timmel, C. R. Delocalisation of Photoexcited Triplet States Probed by Transient EPR and Hyperfine Spectroscopy. *J. Magn. Reson.* **2017**, *280*, 103−116.

(52) Cohen, A. E. Nanomagnetic Control of Intersystem Crossing. *J. Phys. Chem. A* **2009**, *113* (41), 11084−11092.

(53) Koptyug, A. V.; Saik, V. O.; Animisov, O. A.; Molin, Y. N. Spin-Locking in Concentration-Narrowed OD ESR Spectra. *Chem. Phys.* **1989**, *138* (1), 173−178.

(54) Wedge, C. J.; Lau, J. C. S.; Ferguson, K.-A.; Norman, S. A.; Hore, P. J.; Timmel, C. R. Spin-Locking in Low-Frequency Reaction Yield Detected Magnetic Resonance. *Phys. Chem. Chem. Phys.* **2013**, *15* (38), 16043.

(55) Nelson, J. N.; Krzyaniak, M. D.; Horwitz, N. E.; Rugg, B. K.; Phelan, B. T.; Wasielewski, M. R. Zero Quantum Coherence in a Series of Covalent Spin-Correlated Radical Pairs. *J. Phys. Chem. A* **2017**, *121* (11), 2241−2252.

(56) Benduhn, J.; Tvingstedt, K.; Piersimoni, F.; Ullbrich, S.; Fan, Y.; Tropiano, M.; McGarry, K. A.; Zeika, O.; Riede, M. K.; Douglas, C. J.; Barlow, S.; Marder, S. R.; Neher, D.; Spoltore, D.; Vandewal, K. Intrinsic Non-Radiative Voltage Losses in Fullerene-Based Organic Solar Cells. *Nat. Energy* **2017**, *2* (6), 17053.

(57) Liu, S.; Yuan, J.; Deng, W.; Luo, M.; Xie, Y.; Liang, Q.; Zou, Y.; He, Z.; Wu, H.; Cao, Y. High-Efficiency Organic Solar Cells with Low Non-Radiative Recombination Loss and Low Energetic Disorder. *Nat. Photonics* **2020**, *14* (5), 300−305.

(58) Miller, O. D.; Yablonovitch, E.; Kurtz, S. R. Strong Internal and External Luminescence as Solar Cells Approach the Shockley−Queisser Limit. *IEEE J. Photovoltaics* **2012**, *2* (3), 303−311.

(59) Liu, Z.; Krückemeier, L.; Krogmeier, B.; Klingebiel, B.; Márquez, J. A.; Levcenko, S.; Öz, S.; Mathur, S.; Rau, U.; Unold, T.; Kirchartz, T. Open-Circuit Voltages Exceeding 1.26 V in Planar Methylammonium Lead Iodide Perovskite Solar Cells. *ACS Energy Lett.* **2019**, *4* (1), 110−117.

(60) Qian, D.; Zheng, Z.; Yao, H.; Tress, W.; Hopper, T. R.; Chen, S.; Li, S.; Liu, J.; Chen, S.; Zhang, J.; Liu, X.-K.; Gao, B.; Ouyang, L.; Jin, Y.; Pozina, G.; Buyanova, I. A.; Chen, W. M.; Inganäs, O.; Coropceanu, V.; Bredas, J.-L.; Yan, H.; Hou, J.; Zhang, F.; Bakulin, A. A.; Gao, F. Design Rules for Minimizing Voltage Losses in High-Efficiency Organic Solar Cells. *Nat. Mater.* **2018**, *17* (8), 703−709.

(61) Chen, X.-K.; Qian, D.; Wang, Y.; Kirchartz, T.; Tress, W.; Yao, H.; Yuan, J.; Hülsbeck, M.; Zhang, M.; Zou, Y.; Sun, Y.; Li, Y.; Hou, J.; Inganäs, O.; Coropceanu, V.; Bredas, J.-L.; Gao, F. A Unified Description of Non-Radiative Voltage Losses in Organic Solar Cells. *Nat. Energy* **2021**, *6* (8), 799−806.

(62) Vandewal, K.; Mertens, S.; Benduhn, J.; Liu, Q. The Cost of Converting Excitons into Free Charge Carriers in Organic Solar Cells. *J. Phys. Chem. Lett.* **2020**, *11* (1), 129−135.

(63) Coropceanu, V.; Chen, X.-K.; Wang, T.; Zheng, Z.; Brédas, J.-L. Charge-Transfer Electronic States in Organic Solar Cells. *Nat. Rev. Mater.* **2019**, *4* (11), 689−707.

(64) Karki, A.; Gillett, A. J.; Friend, R. H.; Nguyen, T.-Q. The Path to 20% Power Conversion Efficiencies in Nonfullerene Acceptor Organic Solar Cells. *Adv. Energy Mater.* **2021**, *11* (15), 2003441.

(65) Zampetti, A.; Minotto, A.; Cacialli, F. Near-Infrared (NIR) Organic Light-Emitting Diodes (OLEDs): Challenges and Opportunities. *Adv. Funct. Mater.* **2019**, *29* (21), 1807623.

(66) Gélinas, S.; Rao, A.; Kumar, A.; Smith, S. L.; Chin, A. W.; Clark, J.; van der Poll, T. S.; Bazan, G. C.; Friend, R. H. Ultrafast Long-Range Charge Separation in Organic Semiconductor Photovoltaic Diodes. *Science (80-.).* **2014**, *343* (6170), 512−516.

(67) Eisner, F. D.; Azzouzi, M.; Fei, Z.; Hou, X.; Anthopoulos, T. D.; Dennis, T. J. S.; Heeney, M.; Nelson, J. Hybridization of Local Exciton and Charge-Transfer States Reduces Nonradiative Voltage Losses in Organic Solar Cells. *J. Am. Chem. Soc.* **2019**, *141* (15), 6362−6374.

(68) Chen, X.-K.; Coropceanu, V.; Brédas, J.-L. Assessing the Nature of the Charge-Transfer Electronic States in Organic Solar Cells. *Nat. Commun.* **2018**, *9* (1), 5295.

(69) Lee, J.; Ko, S.-J.; Seifrid, M.; Lee, H.; McDowell, C.; Luginbuhl, B. R.; Karki, A.; Cho, K.; Nguyen, T.-Q.; Bazan, G. C. Design of Nonfullerene Acceptors with Near-Infrared Light Absorption Capabilities. *Adv. Energy Mater.* **2018**, *8* (26), 1801209.

(70) Classen, A.; Chochos, C. L.; Lüer, L.; Gregoriou, V. G.; Wortmann, J.; Osvet, A.; Forberich, K.; McCulloch, I.; Heumüller, T.; Brabec, C. J. The Role of Exciton Lifetime for Charge Generation in Organic Solar Cells at Negligible Energy-Level Offsets. *Nat. Energy* **2020**, *5* (9), 711−719.

(71) Han, G.; Hu, T.; Yi, Y. Reducing the Singlet−Triplet Energy Gap by End-Group Π−π Stacking Toward High-Efficiency Organic Photovoltaics. *Adv. Mater.* **2020**, *32* (22), 2000975.

(72) Yuan, J.; Zhang, Y.; Zhou, L.; Zhang, G.; Yip, H.-L.; Lau, T.-K.; Lu, X.; Zhu, C.; Peng, H.; Johnson, P. A.; Leclerc, M.; Cao, Y.; Ulanski, J.; Li, Y.; Zou, Y. Single-Junction Organic Solar Cell with over 15% Efficiency Using Fused-Ring Acceptor with Electron-Deficient Core. *Joule* **2019**, *3* (4), 1140−1151.

(73) Zhang, G.; Chen, X.-K.; Xiao, J.; Chow, P. C. Y.; Ren, M.; Kupgan, G.; Jiao, X.; Chan, C. C. S.; Du, X.; Xia, R.; Chen, Z.; Yuan, J.; Zhang, Y.; Zhang, S.; Liu, Y.; Zou, Y.; Yan, H.; Wong, K. S.; Coropceanu, V.; Li, N.; Brabec, C. J.; Bredas, J.-L.; Yip, H.-L.; Cao, Y. Delocalization of Exciton and Electron Wavefunction in Non-Fullerene Acceptor Molecules Enables Efficient Organic Solar Cells. *Nat. Commun.* **2020**, *11* (1), 3943.

(74) Wang, R.; Zhang, C.; Li, Q.; Zhang, Z.; Wang, X.; Xiao, M. Charge Separation from an Intra-Moiety Intermediate State in the High-Performance PM6:Y6 Organic Photovoltaic Blend. *J. Am. Chem. Soc.* **2020**, *142* (29), 12751−12759.

(75) Liu, Q.; Smeets, S.; Mertens, S.; Xia, Y.; Valencia, A.; D'Haen, J.; Maes, W.; Vandewal, K. Narrow Electroluminescence Linewidths for Reduced Nonradiative Recombination in Organic Solar Cells and Near-Infrared Light-Emitting Diodes. *Joule* **2021**, *5* (9), 2365−2379.