

Dark-triplet-induced instability and efficiency roll-off in blue phosphorescent organic light-emitting devices

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The relative instability of high-efficiency blue phosphorescent organic light-emitting devices (OLEDs) is an important and longstanding challenge. Conventional models of degradation emphasize the dynamics of emissive triplet excitons on phosphorescent molecules, neglecting the potential role of nonemissive, “dark,” triplet excitons on host and charge blocking molecules. Bright and dark triplet dynamics are probed *in situ* using surface plasmon polariton-coupled modulation and magnetic exciton annihilation modulation, respectively. It is observed that dark triplet excitons dominate both the instability and efficiency roll-off of a high-performance blue phosphorescent OLED. Dissociating dark triplets both improves device stability and reduces efficiency losses at high brightness by a factor of 2. The combined benefit to stability of Purcell engineering and dark triplet management is a factor of 3.5. The results demonstrate that dark triplet excitons reduce the potential benefit of Purcell engineering, emphasizing the importance of *in-situ* characterization and control of dark triplets to realize the goal of stable blue phosphorescent OLEDs.

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I. INTRODUCTION

High-efficiency organic light-emitting devices (OLEDs) harness energy stored in spin-1 “triplet” excited states, or excitons. Triplets are typically long-lived dark states, with spin-disallowed emission. To harness their energy for electroluminescence, phosphorescent OLEDs use heavy metals such as Pt or Ir to mix triplet states with spin-0 “singlets” [1–6], allowing light emission directly from the triplet [7]. Exciton radiative lifetimes in such devices are typically on the order of microseconds [1], roughly 1000× longer than the radiative lifetimes in a typical fluorescent OLED, with a corresponding increase in the energy density stored within the device. Long exciton lifetimes also exacerbate the probability of collisions with another excited state or charge, known as triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA),

respectively [8–11]. Triplet annihilation in blue OLEDs generates high-energy states carrying up to 6 eV—large enough to break intramolecular bonds—and has been identified as an important contributor to OLED instability [12].

Phosphorescent technologies are presently used to generate green and red colors in OLED displays. But realizing a stable high-efficiency blue OLED remains an outstanding problem. One proposed solution is “Purcell enhancement,” which increases the rate of light emission to better compete with triplet annihilation processes, thereby enhancing stability and minimizing efficiency losses [13]. Indeed, significantly improved stability has been realized by reducing phosphorescent lifetimes in an optical study by Ha *et al.* [13] as well as prior work on OLEDs [14,15]. OLED studies, however, have shown that changes in the lifetime of emissive “bright” triplets do not simply correlate with the observed efficiency “roll-off” [9], as might be expected for phenomena dependent on the annihilation of bright triplets. Indeed, studies of OLED efficiency ascribe a dominant role to “dark” losses that are expected to be immune to Purcell engineering because they do not involve bright triplets [9].

In this work, we investigate “dark” processes in blue phosphorescent OLEDs and their role in device instability. We show that conventional models of blue phosphorescent

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OLEDs are incomplete in their neglect of long-lived, “dark” triplets that can accumulate on host and charge blocking materials. We demonstrate experimental techniques to identify dark triplets within operating OLEDs, and we show that unless they are deliberately managed, dark triplets can dominate the dynamics of degradation and efficiency roll-off. In particular, we analyze exciplex hosts, which are observed to improve the performance of some blue phosphorescent devices [6]. Although the role of exciplex hosts is sometimes described as improving “charge balance,” we find that the reduction of bright triplet quenching by more evenly-distributed charges cannot explain the full device impact of exciplex hosts. Instead, we determine that exciplex hosts quench dark triplets, approximately doubling the potential benefit of Purcell engineering of bright triplet states. The combination of Purcell engineering and the use of exciplex hosts that quench dark triplets is observed to improve the stability of blue OLEDs by a factor of $\times 3.5$.

II. EXPERIMENTAL DESIGN

A. Exciton dynamics

A model of exciton dynamics in phosphorescent OLEDs is shown in Fig. 1(a). In the ideal case, injected charge either recombines directly on phosphorescent molecules or generates excitons in the host that quickly transfer to phosphorescent molecules, thereby generating emissive triplet excitons and ultimately producing light. Annihilation reactions involving bright triplets compete with light emission, causing degradation and efficiency losses [11,13–15]. To quantify how the rate of annihilation reactions is impacted

by changes in the bright triplet lifetime, we seek experimental isolation of the latter. As schematically shown in Fig. 1(b), bright triplet lifetimes can efficiently be modulated by near-field coupling to polaritonic acceptor modes at nearby dielectric-metal interfaces [13]. Thus, OLED cathodes with common electrical properties but externally varied optical characteristics [16,17] can be used to implement surface plasmon polariton modulation (SPPM) of the bright triplet lifetime to determine its impact on device stability and efficiency roll-off.

As discussed below, conventional models of OLED degradation typically neglect excited states on host or charge blocking molecules because such triplet states are expected to be rapidly harvested by the phosphor [7,8]. These excitons are nonemissive, “dark” states and difficult to probe due to their inefficient phosphorescent decay. To detect the presence of dark excitons, we note that the differing properties of bright and dark triplet excitons are related to the splitting of the triplet sublevels at zero magnetic field. Dark triplets have a small zero field splitting (ZFS) of ~ 10 μeV due to the absence of appreciable spin-orbit coupling. Strong spin-orbit coupling on phosphors, however, yields much larger ZFS of ~ 1 – 100 meV [18]. Thus, moderate magnetic fields ($B < 0.4$ T) modulate TPA and TTA processes that only involve dark triplets, while the dynamics of bright triplets are unaffected. Consequently, we employ magnetic exciton annihilation modulation (MEAM) to probe for the presence of dark triplets, allowing us to nondestructively obtain spectroscopic signatures of annihilation events involving dark triplet states. In Fig. 1(c), we show representative magnetic field dependencies of TPA and TTA following Merrifield theory [19].

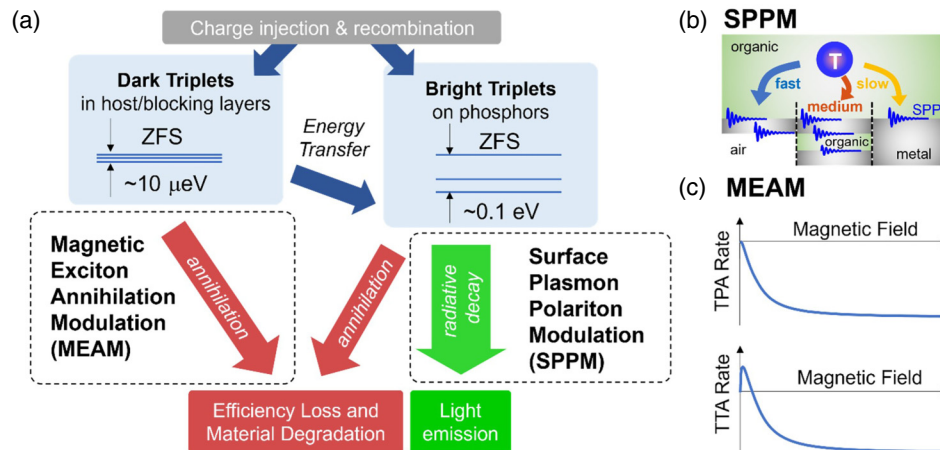


FIG. 1. (a) Schematic model of exciton dynamics in OLEDs. Bright and dark triplets are distinguished by their phosphorescent efficiency and the ZFS of their triplet sublevels. (b) The dynamics of bright triplets are probed by SPPM, where we vary coupling to an SPP mode, thereby modulating the overall lifetime of the bright triplet. (c) “Dark”, nonemissive, excitons on organic host or blocking layers are studied by MEAM, which modulates the rate of TPA and TTA. Both TPA and TTA have characteristic dependencies on the applied magnetic field, as shown here.

If triplets interact in a TTA process, the combination of two triplets has nine possible spin states: one singlet, three triplets, and five quintets. The quintets can mix with the singlet because these species have the same symmetry under exchange. An applied magnetic field alters the rate of TTA by varying the distribution of singlet character in the mixed singlet-quintet states. The pure quintet is energetically inaccessible; thus the singlet character controls the rate of TTA. Note that the triplet TT pairs are unaffected by the field because they do not mix with singlets or quintets.

At zero field, three states have some singlet character; at high field, two states have singlet character [19]. If we assume that the nine TT pairs are populated randomly, then the overall trend is that the applied magnetic field slows down the TTA process. At intermediate fields, however, there can be degeneracies, which increase the number of states with some singlet character [19]. This increases the TTA rate at low fields and yields a zero crossing in the overall TTA characteristic. The zero crossing is the distinctive signature of a TTA process.

The interaction of triplets and charges is simpler. The initial system has total spin of $3/2$ and consists of a

quartet and a doublet [20]. After annihilation the total spin is $1/2$. The magnetic field systematically decreases the number of initial states with doublet character, reducing the rate of triplet-charge annihilation. Thus, triplet-charge annihilation slows monotonically with applied magnetic field.

B. Device structures

Both SPPM and MEAM techniques can be employed *in situ* to determine the relative impact of bright and dark triplets on degradation and efficiency roll-off phenomena within operating OLEDs. Experimentally, we consider blue phosphorescent devices based on a tetradentate Pt(II) emitter, platinum(II) [6-(2,3-dihydro-3-(3,5-di-*tert*-butylphenyl)-1*H*-benzo[*d*]imidazol-1-ylidene- κ C²)-1,2-phenylene- κ C¹]oxy[9-(4-*tert*-butylpyridin-2-yl- κ N)-9*H*-carbazole-1,2-diyl- κ C¹] (PtON5-dbp-tBu/PtON-TBBI) [6]. This class of emitters was introduced by Jian Li and co-workers [4,5] and has demonstrated outstanding stability and efficiency in devices [6,21]. Rather engineering our OLEDs for maximum efficiency as in the previous work [6,21], we build OLEDs as shown in Fig. 2(a), with three different cathode structures used to probe the bright triplets using

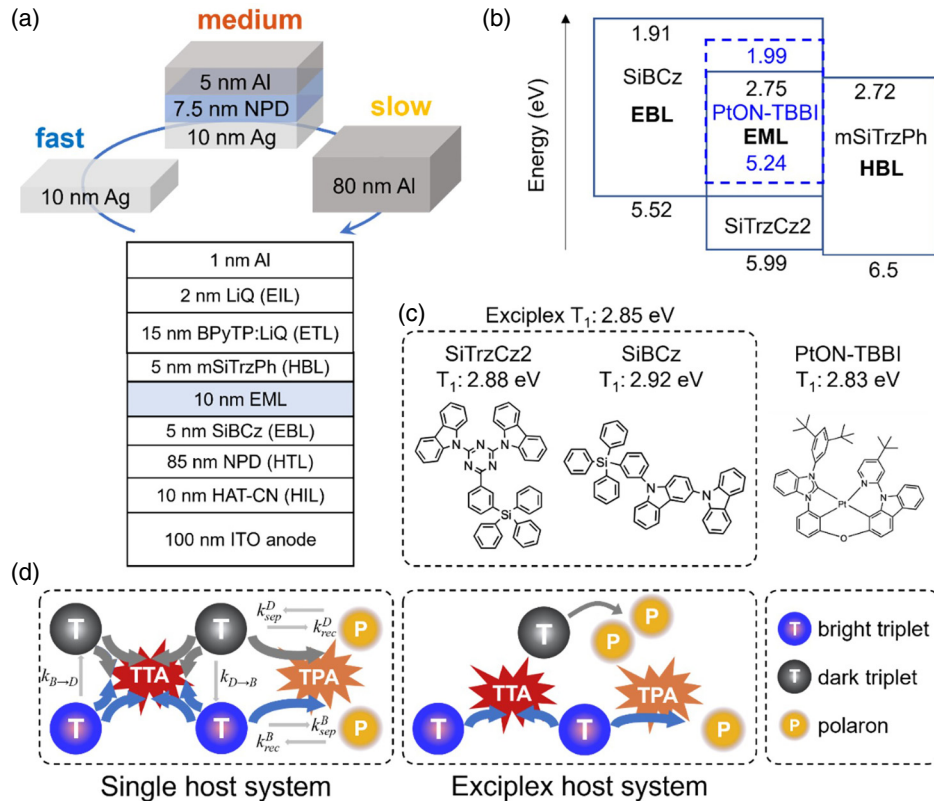


FIG. 2. (a) Blue phosphorescent OLED structure with three cathodes used to modulate coupling to surface plasmon polaritons in SPPM studies. We label them “fast,” “medium,” and “slow,” according to the coupling rate. (b) Energy levels in the emissive layer and adjacent charge blocking layers from Sun *et al.* [6]. (c) Key emissive, host and charge blocking molecules with triplet energies obtained by Sun *et al.* [6]. (d) The expected triplet dynamics in single-host and exciplex-host EMLs. The exciplex host dissociates dark triplets.

SPPM. Each cathode possesses different surface plasmon polariton (SPP) properties to modulate the bright triplet lifetime, but all OLEDs possess an identical organic layer composition and identical charge injection interfaces. Indeed, we demonstrate in Appendix A that the stability of the OLEDs in this work is sensitive to the position of the recombination zone. Moving the location of the recombination zone significantly alters the “charge balance” and cannot be used in these devices to assess the impact of varying the exciton lifetime.

We quantify the optical properties of the three cathodes below, categorizing them as “fast,” “medium,” and “slow.” As shown in Fig. 2(a), the fast cathode consists of a 10-nm-thick Ag layer on top of the injection interface; the medium cathode has a 10-nm-thick film of Ag on top of the injection interface with an added stack of 7.5 nm of *a*-NPD and 5 nm of Al. This additional interface slightly reduces coupling strength by hybridization of adjacent surface plasmon modes [17]. The slow cathode is an 80-nm-thick film of Al exhibiting the weakest coupling strength on top of the injection interface.

Within the OLED, we employ SiBCz as an electron blocking layer and hole transporting host. SiTrzCz2 is used as an electron transporting host with hole blocking provided by mSiTrzPh. The emissive layer (EML) consists of either a single host or an exciplex host. The single-host EML consists of 10 wt. % PtON-TBBI doped into 90% SiBCz. The exciplex host EML is composed of 10% PtON-TBBI:60% SiBCz:30% SiTrzCz2. The charge transport levels obtained by Sun *et al.* [6] for the EML and electron and hole blocking layers are shown in Fig. 2(b). The molecular structures of the materials in the emissive layer are shown in Fig. 2(c) together with their triplet excited state energies obtained experimentally from low-temperature phosphorescence by Sun *et al.* [6].

The exciplex host introduces SiTrzCz2 in the EML adding an additional electron transport level. While increasing manufacturing complexity, exciplex hosts have been shown to significantly improve operational stability [6,21–23]. This has been predominantly ascribed to the separation of charge transport onto two host species as well as reduced charge trapping and a widened recombination zone [21]. In this work, however, we examine the impact of exciplex hosts on dark triplets in the EML. Indeed, as confirmed by the expected energy levels shown in Fig. 2(b), exciplex host systems are expected to aid in the dissociation of any dark triplets formed within the EML because the weakly bound donor-acceptor charge transfer state in the exciplex host has a lower energy than the host triplet states.

C. Theory and simulation

To formulate theoretical expectations for exciton lifetime modulations, we solve for the electromagnetic field

inside the OLED using dyadic Green’s functions to calculate the coupling strength of bright triplets to surface plasmon polaritons at the organic-cathode interface [16], as shown in Fig. 8. We confirm that modulation of the bright triplet lifetime is independent of other device characteristics through examination of the current-voltage characteristics in Fig. 10. We summarize the modulation by its associated quenching factor $QF = \tau_0/\tau$, where τ_0 is the exciton lifetime in vacuum, and τ is the exciton lifetime in the OLED. Integrating the calculated radiative and non-radiative rates over the emission spectrum of PtON-TBBI yields expected quenching factors of $QF = 3.1, 2.2$, and 1.3 for the fast, medium, and slow devices, respectively.

We construct two kinetic models to analyze blue phosphorescent OLED stability and efficiency roll-off: a “minimal” model taking into account only bright triplets and charges, and a “combined” model adding dark exciton interactions. Specifically, the “combined” model supplements a conventional “minimal” OLED kinetic model by considering interconversion between dark and bright triplets, with rates $k_{D \rightarrow B}$ and $k_{B \rightarrow D}$, as well as interconversion of dark triplets and polarons, with rates k_{sep}^D and k_{rec}^D . Bimolecular triplet-triplet k_{TTA} and triplet-polaron k_{TPA} annihilation losses are applied to dark triplets with the same constants used for bright triplets:

$$\begin{aligned} \frac{dT_D}{dt} = & k_{B \rightarrow D} T_B - (k_{D \rightarrow B} + k_{sep}^D) T_D + k_{rec}^D P^2 \\ & - k_{TTA} T_B T_D - k_{TTA} T_D^2 - k_{TPA} T_D P, \end{aligned} \quad (1)$$

where P is the polaron density, T_B and T_D are the densities of bright and dark triplets, respectively, and the unimolecular rates are in units s^{-1} and the bimolecular rates $nm^3 s^{-1}$. A detailed description of the complete models and fitting approach is found in Appendices D and E. Schematic applications of the “combined” model to a single-host device and the “simple” model to an exciplex host device are shown in Fig. 2(d).

III. METHODS

A. Device fabrication

In-house fabricated and patterned indium tin oxide (ITO) was used as the substrate for OLED growth. The ITO was cleaned by manual scrubbing with detergent for 10 min. Substrates were then sequentially cleaned in two baths of deionized water, two baths of acetone, and two baths of isopropyl alcohol, each for 15 min under ultrasonication. Organic materials were synthesized in-house or provided by Universal Display Corporation. Layer deposition was carried out in a thermal evaporator at high-vacuum pressure below 5×10^{-8} Torr. Organic layers were deposited at a rate of $0.3 \text{ \AA s}^{-1}$; metal layers were deposited at a rate of $1.4 \text{ \AA s}^{-1}$. In-detail documentation

of the fabrication process with all processing parameters can be found at <https://www.fabublox.com/process-editor/e2eaad12-b774-47f7-b90d-f47897a57d4a>.

B. Characterization

OLED current-voltage characterization was carried out using a Keithley source measure unit (SMU), and luminance was detected using a calibrated silicon photodiode. All devices were measured in a nitrogen atmosphere with oxygen and moisture levels below 1 ppm immediately after device fabrication. Degradation measurements were carried out on as-fabricated devices in the same nitrogen environment without any prior current-voltage sweeps.

Time-correlated single photon counting (TCSPC) was carried out on a PicoHarp 300 TCSPC module. Sample excitation was carried out at $\lambda = 405$ nm with a PicoQuant LDH-P-C-405 with a less than 90 ps pulse duration. Photon detection used a single-photon avalanche photodiode (MPD PDM Series, 50 μm). The setup's instrument response function (IRF) was 64 ps. All samples measured with TCSPC in this work were excited at a 125 kHz laser repetition rate and base excitation power of 500 nW. Excitation power was adjusted to keep emission signal constant for all devices of varying cathode reflectivity. Reference measurements at half and double the excitation density were taken to ensure obtained triplet exciton lifetimes were excitation-power independent. Triplet exciton lifetimes, τ , were obtained by fitting to a simple monoexponential

decay function of the form $\text{PL} = a \cdot \exp(t/\tau)$, where t is time and a is a constant.

For magnetic field effect (MFE) measurements, fabricated OLEDs were encapsulated *in situ* under a nitrogen atmosphere (<1 ppm H_2O and O_2) using a piece of glass adhered to the substrate with an ultraviolet-cured adhesive OG159-2 purchased from Epoxy Technology Inc. MFE measurements were then carried out in a water-cooled electromagnet model 3470 by GMW Magnet Systems. Samples were placed in a gap of about 1.5 inches (37 mm) between the two magnet poles, yielding a maximum magnetic strength of about 0.4 T. Constant current was applied to devices using a Keithley SMU. Electroluminescence was detected with a silicon photodetector 818-SL by Newport connected to a lock-in amplifier (SR830, Stanford Research Systems) to maximize signal-to-noise ratio.

IV. RESULTS AND DISCUSSION

A. Surface plasmon polariton modulation

Figures 3(a) and 3(b) show transient photoluminescence data of the single and exciplex host device sets, respectively, obtained by TCSPC for the devices with a single host. After excluding the background fast fluorescent decay, phosphorescent emission approaches monoexponential decay for all three device variations. Relative to the fast device, the experimental QF ratios for the slow and medium devices are 2.2 and 1.3, in close agreement with the calculated QF ratios of 2.4 and 1.4, respectively.

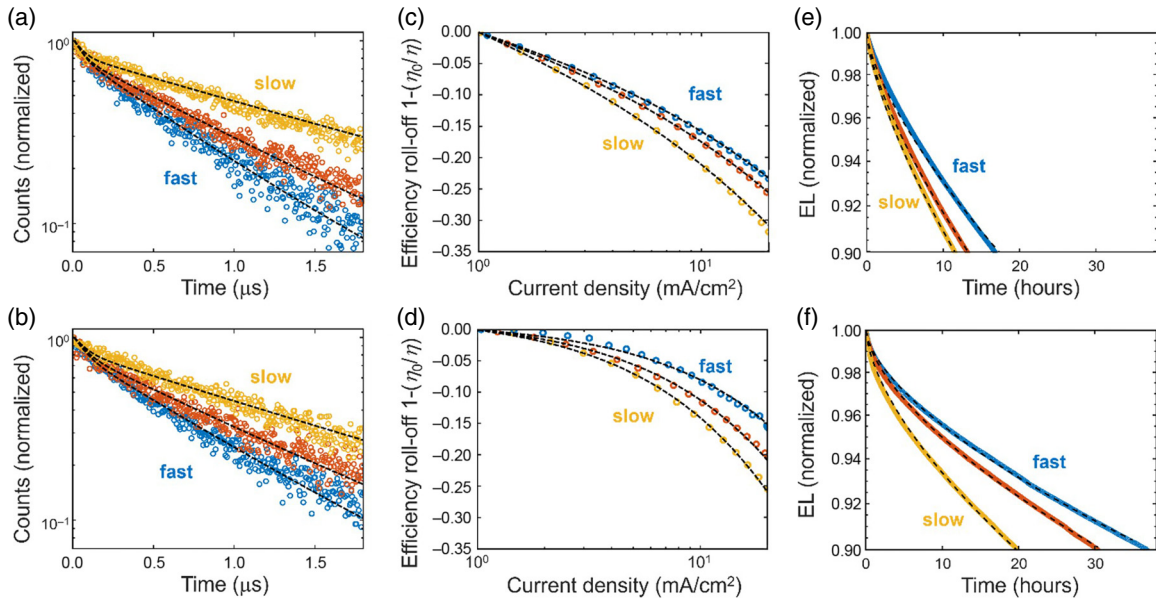


FIG. 3. Transient photoluminescence of (a) single and (b) exciplex host OLEDs with “fast,” “medium,” and “slow” cathodes shown in Fig. 2. External quantum efficiency roll-off for (c) single and (d) exciplex host OLEDs with “fast,” “medium,” and “slow” cathodes. Electroluminescent degradation under constant current density, $J = 5 \text{ mA cm}^{-2}$, for (e) single and (f) exciplex host OLEDs with “fast,” “medium,” and “slow” cathodes. Data corresponding to “medium” cathodes are shown in red but unlabeled. Black lines show the result of (a)–(d) fitting using a kinetic modeling and (e)–(f) a stretched exponential model.

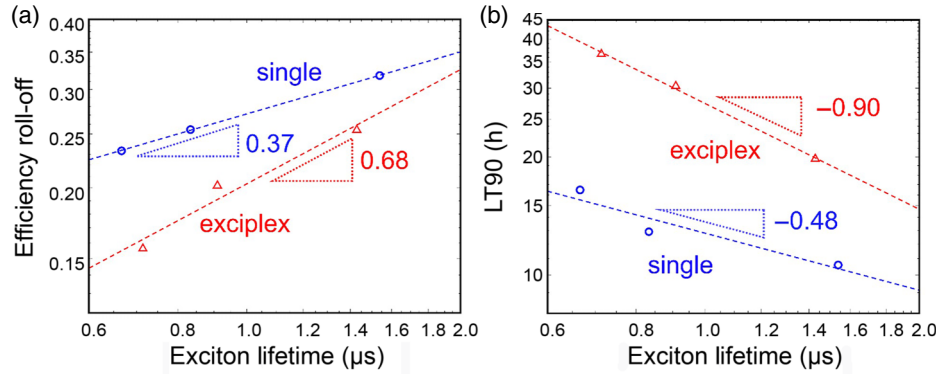


FIG. 4. (a) A log-log plot of external quantum efficiency roll-off losses versus lifetime of bright excitons for both single and exciplex hosts. The dependence on bright exciton lifetime is much stronger for exciplex hosts. (b) A log-log plot of electroluminescence aging for devices operated at a constant current density of 5 mA cm^{-2} . Again, the dependence on bright exciton lifetime is much stronger for exciplex hosts.

Similarly, the measured QF ratios for the exciplex devices are 1.8 and 1.3, respectively. Both transient photoluminescence device sets are well fitted using a minimal kinetic model.

In Fig. 3(c), we characterize the impact of the bright triplet lifetime on efficiency roll-off of the single-host devices. The external quantum efficiency η of an OLED typically decreases with increasing current density J as the rate of bright triplet annihilation events $k_{\text{loss}}(J)$ increases. We define the efficiency roll-off $\Delta\eta$ as $\Delta\eta = 1 - \eta_0/\eta(J)$, where $\eta_0/\eta(J)$ is the ratio of peak external quantum efficiency η_0 to the efficiency η at a given current density J . Notably, as derived in Appendix G, $\Delta\eta = -\tau k_{\text{loss}}(J)$. In other words, the efficiency roll-off is expressed here such that it is expected to scale at least linearly with the triplet exciton lifetime, τ . As shown in Fig. 4(a) in blue, however, the observed dependence is significantly smaller for the single-host devices, exhibiting a less than square-root dependence on τ , showing a slope of 0.37 on a log-log scale, extracted at $J = 20 \text{ mA cm}^{-2}$. Unlike previous studies [9], the discrepancy with theory cannot be explained by variations in charge carrier balance because $\Delta\eta$ is compared across devices at constant current density. Instead, the data strongly suggest that models based solely on bright triplets are incomplete. This hypothesis is supported by the kinetic modeling described above. Despite a high degree of flexibility, the best-fit minimal models result in a relatively large root mean square error (RMSE) in the roll-off (see Fig. 14), but even the simplest combined dark exciton model reduces the error 8-fold, resulting in a fit that is indistinguishable from the experimental data, as overlaid in Fig. 3(c). The obtained rate constants are given in Table II of Appendix E, and representative rate constants with lowest error values for each model are presented in Table I.

Next, we compare device stabilities by extracting LT90s at a constant current density of $J = 5 \text{ mA cm}^{-2}$ for all three

device variations, as shown in Fig. 3(e). The stability trend follows expectations, with the three devices featuring a single host yielding LT90's of 16.5 h, 12.9 h, and 10.6 h, for the fast, medium, and slow devices, respectively. Degradation data is fitted using an empirical stretched exponential model [24] of the form $L/L_0 = \exp(-t/\Gamma)^\beta$, where L/L_0 is the ratio of electroluminescence L at a given time t to the electroluminescence at the beginning L_0 . All three curves can be fitted with an identical $\beta = 0.7$, differing only in the time constant Γ . Quantitatively, the dependence of LT90 on triplet lifetime is expected to scale with a power law exponent between 2 and 3.5 depending on the dynamics of the dominant bimolecular process within the OLED [13]. But comparing LT90's on a log-log plot against τ of single-host OLEDs reveals a slope of only 0.48, reproducing the surprisingly low dependence on τ observed for the efficiency roll-off, as shown in Fig. 4(b) in blue. Again, the stability measurements appear inconsistent with models that consider only bright triplet excitons.

Conducting the same analysis for the exciplex host system shows a dependence of roll-off [Fig. 3(d)] and degradation [Fig. 3(f)] rates on triplet lifetime much closer to theoretical expectations. As shown in Fig. 4(a) in red, the dependence of efficiency roll-off on bright triplet lifetime is increased $1.8\times$ in exciplex host devices compared with the single-host devices, exhibiting a power law exponent of 0.68. The link between quenching dark triplets and the increased dependence on bright triplet lifetime is supported by kinetic fitting. The minimal model generates good fits with no significant improvement from including dark triplets, as shown in Table III of Appendix E. Representative rate constants with lowest error values are also shown in Table I.

Similarly, the exciplex devices' LT90's are increased by $2\times$ compared with the single-host devices, yielding 36.7 h, 30.4 h, and 19.8 h for the fast, medium, and slow

TABLE I. Example rate constants from one of many fits to the experimental data for both sets of OLEDs in units s^{-1} or $\text{nm}^3 \text{s}^{-1}$ for the bimolecular rates. Rate constants k_{rad} , k_{sep}^B , and k_{rec}^B are fitted to the experimental photoluminescent data and all other parameters are fit to the experimental roll-off data. Kinetic modeling of single-host devices yields a range of well-fitting but flexible models. Several rate parameters across these models are consistent in value, and others, indicated in parentheses, vary over orders of magnitude while reliably reproducing the data. Such rates are not fully constrained by the experimental data. That is, depending on the kinetic process thought to dominate, there is a model that has the corresponding rate well constrained, while other kinetic processes do not influence the fit. As such we do not report these to be comparable to experiment or literature values. Further discussion of the flexibility of the kinetic modeling is found in Appendices D and E.

OLED	k_{rad}	k_{sep}^B	k_{rec}^B	k_{CL}	k_{TTA}	k_{TPA}	$k_{B \rightarrow D}$	$k_{D \rightarrow B}$	k_{sep}^D	k_{rec}^D
Single host (unconstrained TTA)	Fast: 1.5×10^6 med: 1.2×10^6 Slow: 6.5×10^5	1.9×10^6	2.8×10^9	Fast: 1.4×10^5 med: 1.1×10^8 Slow: 5.3×10^8	(1.4×10^0)	5.0×10^9	3.4×10^5	6.7×10^4	(8.6×10^2)	(6.7×10^5)
Single host (unconstrained TPA)	Fast: 1.5×10^6 Med: 1.2×10^6 slow: 6.5×10^5	1.9×10^6	2.8×10^9	Fast: (4.8×10^5) med: 1.7×10^8 Slow: 6.9×10^8	3.3×10^{10}	(1.5×10^8)	3.3×10^5	5.0×10^4	(6.4×10^{-2})	(5.0×10^1)
Exciplex host	Fast: 1.4×10^6 Med: 1.1×10^6 Slow: 7.0×10^5	1.3×10^6	2.4×10^9	Fast: 5.9×10^5 Med: 9.9×10^7 Slow: 4.7×10^8	3.1×10^{10}	3.8×10^8				

devices, respectively. Similar to the single-host devices, all device variations are fitted well using a stretched exponential model with a single $\beta = 0.64$. Consistent with the roll-off analysis, we observe a nearly $2 \times$ increased dependence of LT90 on τ , exhibiting a slope of 0.90 on a log-log scale, as shown in Fig. 4(b) in red. These results show that both the overall stability and efficiency loss as well as the

impact of Purcell enhancement on stability are improved in the exciplex host system. Nevertheless, the observed dependence on exciton lifetime is still far weaker than obtained in prior optical studies [13] and OLED measurements [15], suggesting that nonradiative states influence degradation mechanisms in this system even for exciplex hosts.

TABLE II. Best total RMSE values and corresponding set of rate constants in units s^{-1} and $\text{nm}^3 \text{s}^{-1}$ for each model fitting to the experimental data of the single-host OLEDs with fast, medium, and slow coupling layers.

RMSE	k_{sep}^B	k_{rec}^B	k_{rad} (fast/medium/slow)				
(a) Models fit to the PL experimental data.							
0.1	1.9×10^6	2.8×10^9	$1.5 \times 10^6/1.2 \times 10^6/6.5 \times 10^5$				
RMSE	k_{TTA}	k_{TPA}	$k_{B \rightarrow D}$	$k_{D \rightarrow B}$	k_{sep}^D	k_{rec}^D	k_{CL} (fast/medium/slow)
(b) Models fit to the roll-off experimental data where the rates in (a) are held fixed. Experimental data does not constrain the parameters in parentheses, which have a range of possible values for the given model.							
11.6	(3.7)	6.5×10^9					
5.5	(3.0)	2.8×10^{10}					4.6×10^9
4.8	(1.8×10^7)	7.7×10^9					$3.2 \times 10^3/1.3 \times 10^8/5.7 \times 10^8$
1.4	(1.5×10^3)	1.1×10^{10}	1.4×10^6	1.4×10^4			
1.4	(9.3)	1.1×10^{10}	1.4×10^6	1.1×10^4	(9.3×10^3)	(1.6×10^{-3})	
1.0	(3.7×10^9)	1.6×10^{10}	6.3×10^5	1.2×10^5			3.8×10^9
0.7	1.0×10^4	6.0×10^9	3.8×10^5	3.6×10^4			$2.0 \times 10^5/8.1 \times 10^7/4.7 \times 10^8$
1.0	(1.9×10^{-8})	1.3×10^{10}	9.7×10^5	1.3×10^4	1.1×10^5	(4.5×10^{-6})	1.8×10^9

TABLE III. Best total RMSE values and corresponding set of rate constants in units s^{-1} and $\text{nm}^3 \text{s}^{-1}$ for each model fitting to the experimental data of the three exciplex host OLEDs with fast, medium, and slow coupling layers.

RMSE	k_{sep}^B	k_{rec}^B	k_{rad} (fast/medium/slow)				
(a) Models fit to the PL experimental data.							
0.1	1.3×10^6	2.4×10^9	$1.4 \times 10^6/1.1 \times 10^6/7.0 \times 10^5$				
RMSE	k_{TTA}	k_{TPA}	$k_{B \rightarrow D}$	$k_{D \rightarrow B}$	k_{sep}^D	k_{rec}^D	k_{CL} (fast/medium/slow)
(b) Models fit to the roll-off experimental data where the rates in (a) are held fixed. Experimental data does not constrain the parameters in paratheses which have a range of possible values for the given model.							
5.1	(1.2×10^3)	2.5×10^9					
1.4	6.7×10^{12}	(6.2×10^6)					(1.1×10^{11})
0.9	3.1×10^{10}	3.8×10^8					$(5.6 \times 10^5)/9.9 \times 10^7/4.7 \times 10^8$
3.0	3.9×10^{10}	(6.5)	1.0×10^6	(7.3×10^{-3})			
1.3	1.1×10^{12}	1.6×10^1	5.9×10^6	1.9×10^6			2.9×10^{11}
0.9	3.1×10^{10}	3.8×10^8	(1.0)	(1.0×10^6)			$(5.6 \times 10^5)/9.9 \times 10^7/4.7 \times 10^8$
3.3	4.6×10^{10}	(1.3×10^6)	8.1×10^5	(1.5×10^{-3})	3.4×10^8	1.8×10^9	
1.3	4.4×10^{11}	(2.7×10^1)	5.5×10^6	2.0×10^6	(3.8×10^{-3})	(4.9×10^{-4})	9.3×10^{10}
0.8	7.0×10^9	(4.0×10^5)	1.3×10^6	(8.1×10^{-4})	9.5×10^5	(1.1)	$(1.4 \times 10^6)/5.0 \times 10^7/2.4 \times 10^8$

B. Magnetic exciton annihilation modulation

To experimentally confirm that the superior performance of exciplex hosts is indeed due to the dissociation of dark excitons, we apply MEAM to electroluminescence from the single-host and exciplex-host OLEDs with identical “fast” cathodes. As discussed above, an applied magnetic field of $B \sim 0.4$ T is expected to significantly perturb the energy levels of dark triplet states, altering annihilation rates for their collisions with charges and other dark triplets, while bright triplet behavior remains unaffected. The MEAM characteristics of the two devices shown in Fig. 5 are notably different. First, the single-host device has a much larger signal overall at low field, which indicates that there are more species with small zero-field splitting interacting with the weak magnetic field in the single-host device. Second, the exciplex host has a monotonic response to the field, while the single host initially gets less efficient before becoming brighter at high field. The differing shape in single and exciplex MEAM indicates that there are different spin-dependent processes that affect electroluminescence in each device.

TPA is known to have a monotonic response to magnetic field, whereas TTA has a nonmonotonic response, which is consistent with the presence of TTA in the single-host device and not the exciplex host [20]. Indeed, through fitting the MEAM data we find a partial TTA signature involving dark triplets in the single-host devices and zero field splitting parameter $D = 40\text{--}60$ μeV as described in Appendix G. The observed dominance of TPA is consistent with previous studies [9–11,25,26]. The positive MEAM trend at high fields confirms that dark triplets largely undergo energy transfer to bright triplets as expected in the model proposed in Fig. 1(a), i.e., reducing the annihilation of dark triplets under a magnetic field increases the electroluminescence from bright triplets.

In contrast, the exciplex host device shows a very weak MEAM signal and no evidence of TTA. We successfully fitted the exciplex host MEAM data with a TPA characteristic defined by $D = 3\text{--}10$ μeV as described in Appendix G. While changes in the host material may cause morphological changes in the spatial distribution of phosphorescent guests and hence changes in the interaction between bright

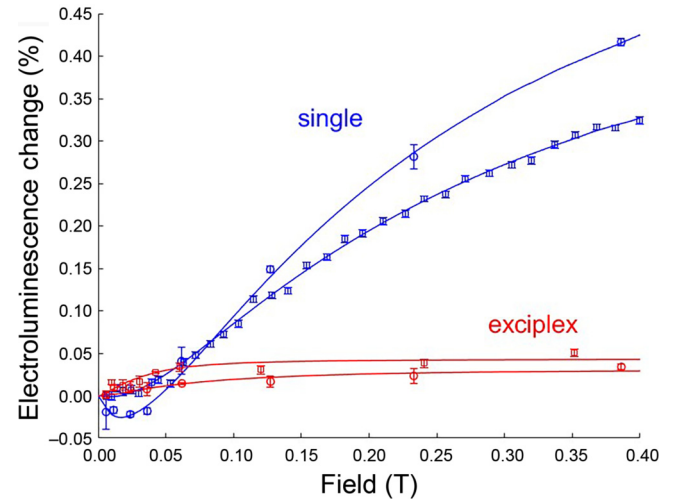


FIG. 5. Magnetic field effects on the electroluminescence from simple and exciplex host OLEDs with “fast” ($\circ$) and “slow” ($\square$) cathodes biased at a current density of $J = 5$ mA cm^{-2} . The single-host OLED exhibits a significantly larger effect. The shape is consistent with TTA between dark triplets. The exciplex host OLED has a much smaller effect, with shape consistent with TPA between dark triplets and charges. The error bars represent standard deviation in each vertical direction, indicating the variations when the device is tested over multiple cycles. Due to a residual 7 mT field in the electromagnet when it is powered off, each curve has been normalized to have zero response at 7 mT.

triplets [27], MEAM detects only dark triplets in the host. We conclude that the exciplex host supports a far lower density of dark triplet states than the single host, resulting in increased stability and reduced roll-off. The MEAM results demonstrate that the increased dependence of roll-off and stability on bright triplet lifetime in the exciplex host devices is linked to an elimination of dark triplets.

V. CONCLUSIONS

Studies of OLED degradation typically consider complex phenomena such as charge balance and its potential impact on triplet annihilation. Subsequent modifications to materials or the device structure seek to demonstrate improved stability. Unfortunately, even if the device stability is observed to improve, it can be difficult to control for complex changes within OLEDs when the materials or structure is modified. The advantage of a technique such as SPPM is that it only modulates phenomena that depend on the density of bright triplets, including bimolecular losses such as TPA or TTA. It follows that observing a very weak dependence on the lifetime of bright triplets, as in the single-host devices of Fig. 3(b), provides conclusive evidence that degradation is driven by other, darker states that are unaffected by modulations in the lifetime of bright triplets.

Phosphorescent molecules within OLEDs are typically expected to quench dark triplets either by energy transfer or by promoting charge transfer and exciplex formation. Blue OLEDs, however, differ from green and red devices because they have notably smaller energetic differences between guest, host, and blocking layer energy levels, thus reducing the probability of host-to-emitter exciton quenching as well as enhancing emitter-to-host back transfer. Indeed, kinetic model fits and characterization using SPPM and MEAM confirm that dark triplets play a crucial role in the efficiency and stability of the studied blue phosphorescent OLEDs.

Although dark triplets may be neglected at low bias, where phosphorescent OLEDs approach unity efficiency, the impact of dark triplets increases at higher current densities, contributing to efficiency roll-off, instability, and other commonly-cited “charge balance” phenomena. In particular, the efficiency roll-off of single-host OLEDs can *only* be modeled by considering dark triplets. The stability of single-host OLEDs is also dependent on dark triplets, exhibiting a weak dependence on the lifetime of bright triplets that contrasts dramatically with prior optical studies [13]. Crucially, this observation is inconsistent with the conventional model of phosphorescent OLED degradation: instability in the single-host devices is *not* dominated by interactions between bright triplets and “unbalanced” charges or other triplets. The exciplex host devices, however, fit conventional kinetic models that ignore dark triplets and exhibit a stronger dependence on the lifetime

of the bright excitons. We attribute these results to destabilization of dark triplets in the exciplex host. This, in turn, contributes to improved efficiency and stability in exciplex host devices and also enhances the attainable benefits of Purcell engineering—one of the most attractive approaches to realizing stable, high-efficiency blue phosphorescent OLEDs. Relative to the conventional “slow” single-host control, the combined benefit of Purcell engineering and reduction of dark triplets provides a $\times 3.5$ improvement in device stability.

The dark triplet interpretation of dynamics in single-host blue phosphorescent OLEDs is supported by MEAM measurements that observe the presence of annihilation interactions between dark triplets, confirming that dark triplets are present in densities sufficient to support bimolecular annihilation. The density of dark triplets is significantly reduced by the exciplex host, with a corresponding decrease in the magnetic field signature. Indeed, we show here that *in-situ* magnetic field modulation of dark triplet interactions is an especially promising tool for characterizing and controlling dark triplets in the quest for more stable blue phosphorescent OLEDs.

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JT, MB, and JL conceived the project and wrote the manuscript. Device fabrication, J-V characterization, and degradation measurements were carried out by AS and CP under the guidance of JL. Green’s functions analysis was performed by JS. MEAM measurements were performed by JT and JS. TCSPC measurements were carried out by JT and WZ. ON and JT developed the theoretical model for roll-off. ON derived theoretical Merrifield models, conceived the code, and performed MEAM analysis. RH and AR derived kinetic models, implemented code, and carried out calculations under the guidance of TV. PS and TL helped with fabrication process development under guidance of FN and MB, respectively. JWP helped with device

fabrication. All authors discussed the results presented in this manuscript.

DATA AVAILABILITY

The data that support the findings of this article are openly available [34].

APPENDIX A: OLED STABILITY AS A FUNCTION OF POSITION OF RECOMBINATION ZONE

Starting from the “fast” OLED design in Fig. 2, we vary the position of the EML by adjusting the thickness of the electron transport layer (ETL) in four different devices: ETL = 15 nm, 20 nm, 25 nm, and 30 nm. The overall thickness of the OLED is preserved by simultaneously thinning the hole transport layer in each device: HTL = 85 nm, 80 nm, 75 nm, and 70 nm. The device structures are summarized in Fig. 6(a). All devices use the same “fast” cathode and a single-host material rather than the exciplex host.

We measure the transient response of the phosphorescent emission in these devices. The results are shown in Fig. 6(b). As expected, the transient lifetime increases with increasing separation from the cathode due to reduced rates of quenching by plasmonic modes in the silver cathode. Indeed, movement of the EML has been previously used to study the impact of exciton lifetime on device stability [14].

The corresponding device stability data are shown in Fig. 6(c), measured at a uniform current density of $J = 5 \text{ mA cm}^{-2}$. Again, as expected, a longer transient lifetime is correlated with faster degradation. The stability data are summarized in Fig. 7 and compared with the single-host data from the main text. Moving the position of the EML is observed to generate dramatically different behavior as compared with varying the cathode structure. At least in this material system, shifting the EML confounds the variation in exciton lifetime with varying “charge balance” or “charge leakage” effects. It is evident from the strong apparent power law that the impact of changes in charge balance are much stronger than the changes in exciton lifetime. We conclude that moving the recombination zone is not a generally reliable method for studying the role of exciton lifetime in OLEDs.

APPENDIX B: CALCULATED QUENCHING FACTORS USING DYADIC GREEN’S FUNCTIONS

Expected triplet lifetime modulations inversely proportional to the quenching factors, QF , for the fast, medium, and slow device variations were calculated using Dyadic Green’s functions as described elsewhere [28]. Figure 8 shows QF s against wavelength for the three device variations. Integrating these over the devices’ electroluminescent spectrum, overlaid in Fig. 8, we obtain weighted $QF = 3.1, 2.2, 1.3$ for the fast, medium, and slow devices, respectively.

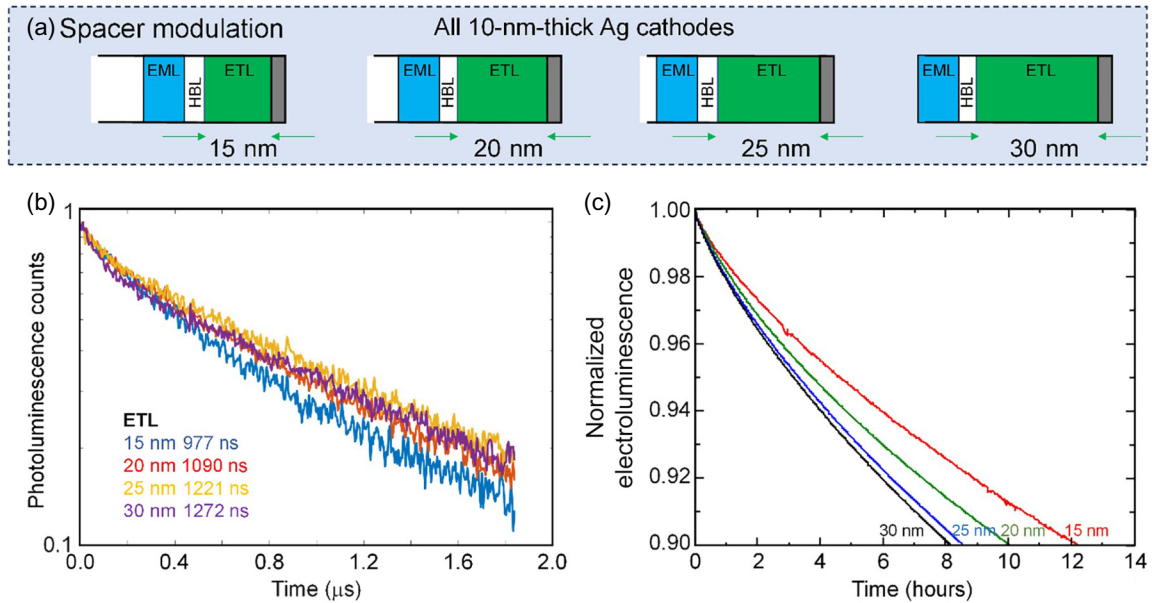


FIG. 6. (a) Device structures employed to study variations in position of the EML. The base structure is the “fast” OLED described in Fig. 2 of the main text. (b) Transient response of the phosphor in each device structure. (c) Electroluminescent stability characterized in each device at a current density of $J = 5 \text{ mA cm}^{-2}$.

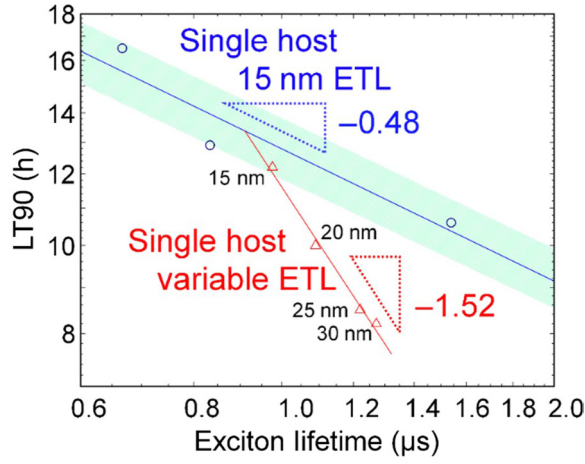


FIG. 7. Dependence of OLED stability on phosphorescent transient lifetime for devices with varying EML position (red triangles). For comparison, we reproduce the “fast,” “medium,” and “slow” SPPM device data from Fig. 4(b) in the main text (black circles). Both device sets use a single-host material rather than the exciplex host. Due to fabrication variability, the “fast” cathode that is common to the set of variable ETL devices exhibits weaker coupling to the cathode and a longer exciton lifetime than the comparable “fast” device in the SPPM set of devices from Fig. 4(b). The two OLED datasets are comparable, however, because all devices with a 15-nm-thick ETL follow a consistent relationship between LT90 and exciton lifetime, represented by the shaded region as a guide to the eye.

The exciton decay rate is modulated by the coupling to the surface plasmon mode. As evident in plots (Fig. 9) of the power dissipation for normalized wavevectors $k_{\parallel}/k_0 > 1$, the thin silver has a particularly localized SPP mode that increases the coupling rate, especially relative to the

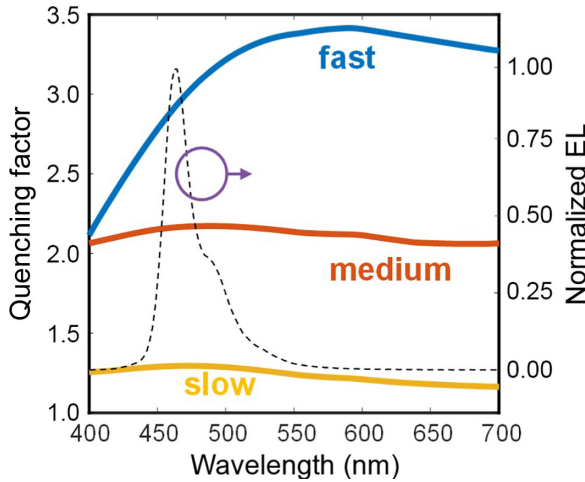


FIG. 8. Calculated quenching factors against wavelength for the fast, medium, and slow device variations overlaid with the fast device’s measured electroluminescent spectrum.

thick aluminum. We designed the “intermediate” cathode with the assumption that two layers of metal should exhibit less localization than the single, thin silver film. Modeling of the coupling is essential to verify the design assumptions [28].

APPENDIX C: OLED CURRENT-VOLTAGE CHARACTERISTICS AND VALIDATION OF THE PROPOSED MODEL

Figure 10 shows current-voltage characteristics of the single and the exciplex host OLEDs with fast, medium and slow cathodes. The current-voltage behavior above turn-on voltage is nearly independent of cathode variation. Luminance is measured through the substrate, and the external quantum efficiency (EQE) for the slow devices is larger than for the other device variations due to strong optical reflections from the thick aluminum cathode. In general, the cathodes sacrifice efficiency light extraction in order to modulate the exciton lifetime. It is also notable that the exciplex host devices exhibit significantly (almost $3\times$) higher efficiency than single-host devices. This is consistent with the conclusion that single-host devices suffer from strong dark triplet losses.

To validate our results, we show device-to-device variation in leakage current and its correlation with EL degradation (Fig. 11). We note that there can be substantial device variation in low-voltage I - V characteristics, even with identical cathodes. This indicates our results are reproducible despite variations in the I - V characteristics at low voltages. Figure 12 shows the operating voltage during OLED degradation experiments. The data show that the voltage rise does not show the same trend with PL lifetime as the luminance loss, further strengthening the attribution of excitonic effects to degradation.

APPENDIX D: KINETIC MODEL DETAILS

1. Kinetic scheme

The species considered in this model include populations of bright triplets (T_B), dark triplets (T_D), and electron (e^-) and hole (h^+) pair charges. Assuming that concentration of electrons and holes are equal (i.e., the system is in perfect charge balance), we consider electrons and holes to be generic “polarons” (P). We only include triplet excitons in this simulation, as singlets radiate on a much faster timescale, which is equivalent to assuming their nonexistence in the model. Additionally, singlets do not typically contribute to the annihilation reactions that lead to roll-off [29,30], so excluding them should not have a significant impact on the conclusions of our model. The processes considered in this set of models, as illustrated in Fig. 13, simulate those occurring in the emitting layer of an OLED during photoluminescence and electroluminescence experiments. In this appendix, we choose to model the number

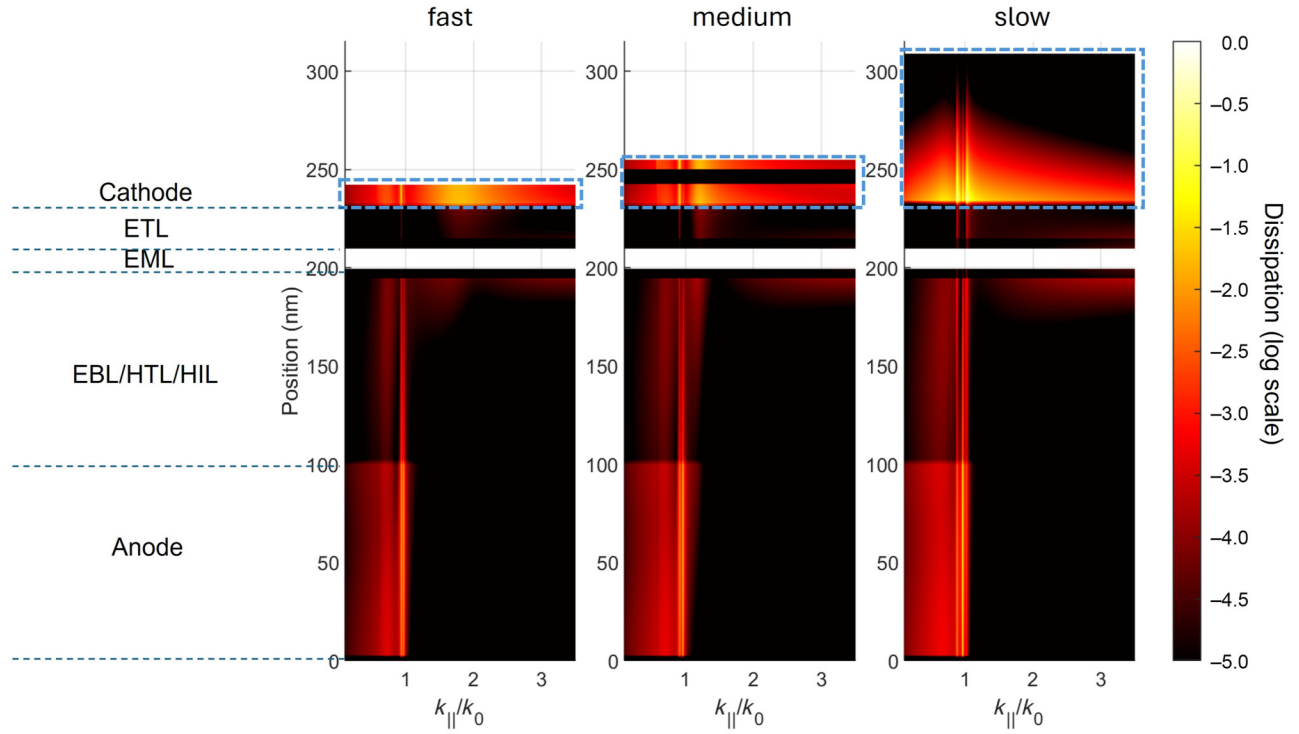
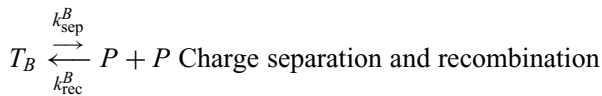
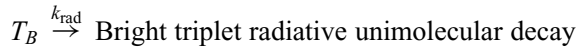


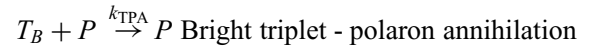
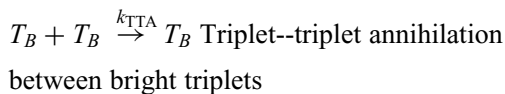
FIG. 9. Absorption of the parallel dipole energy for fast, medium, and slow OLEDs, as a function of the position and normalized surface-parallel wavevector $k_{||}/k_0$. Note especially the localized surface plasmon polariton (SPP) modes with normalized wavevectors $k_{||}/k_0 > 1$. The thin silver has a particularly localized SPP mode. Localization decreases with increasing cathode thickness. The dipole is located at the middle of the EML layer, and the emission wavelength is $\lambda = 460$ nm. The blue dotted box indicates the cathode region.

of species within a 1 nm^3 emitting volume. The processes that govern the dynamics use rate constants with units s^{-1} . To convert to conventional units, as employed in the main text, the population of each species becomes a density (nm^{-3}), and bimolecular rates have units $\text{nm}^3 \text{s}^{-1}$.

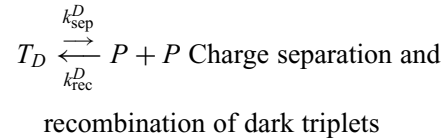
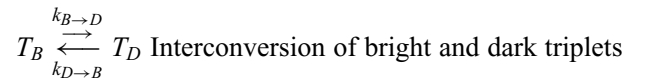
In a “minimal” model, we consider the following processes that govern the populations of bright triplets (T_B) and polarons (P) within the simulation box, where a polaron can be either an electron (e^-) or a hole (h^+):



of bright triplets



Adding a population of dark triplets (T_D) to the minimal model introduces the following processes to build a “combined” model:



In the combined model, the equations describing the annihilation rates are expanded from the minimal model in included interactions between the dark and bright triplets. The triplet-polaron annihilation rate (k_{TPA}) now describes annihilation events between polarons and bright triplets, as well as charges and dark triplets. Similarly, the triplet-triplet annihilation rate (k_{TTA}) now controls the following

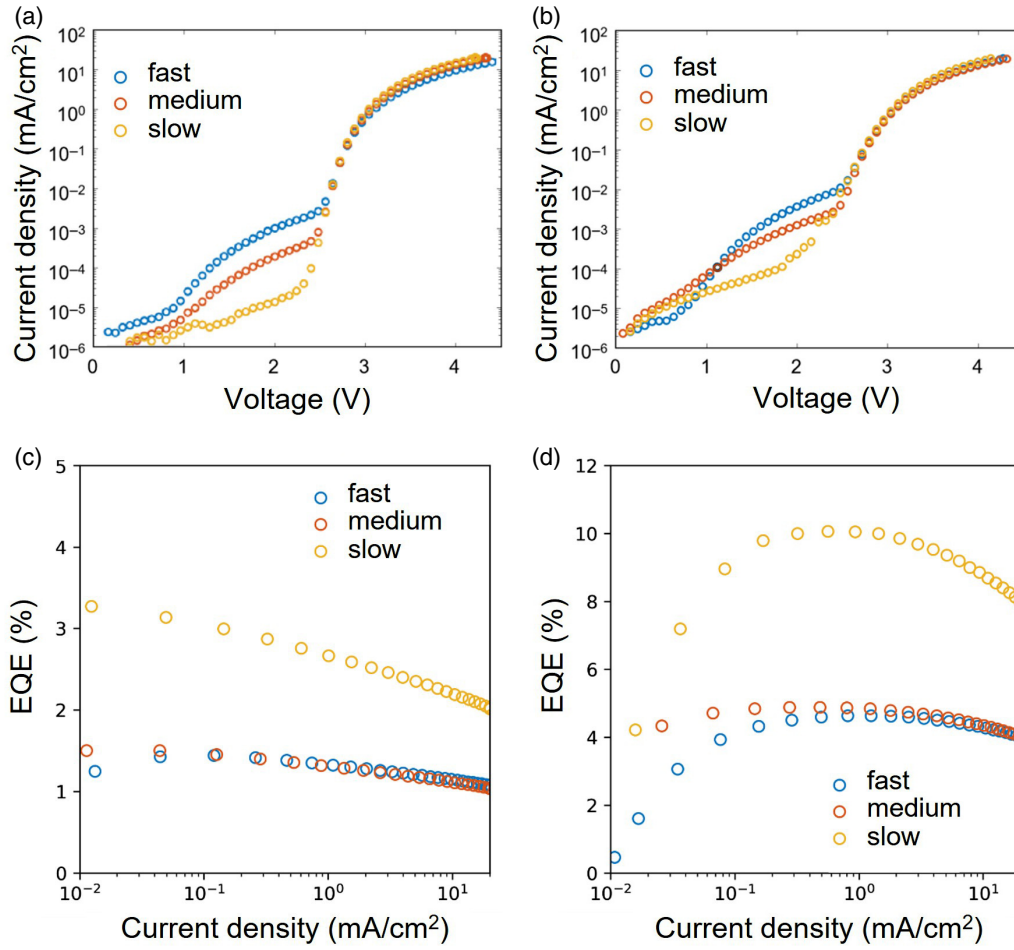
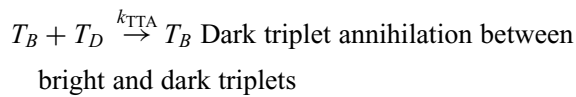
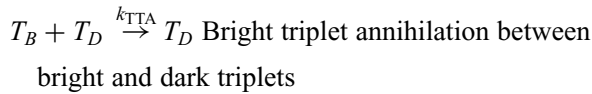
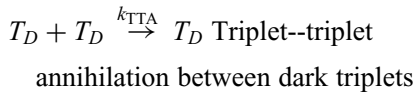
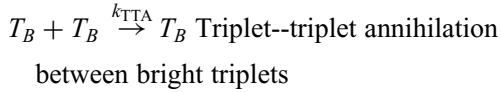


FIG. 10. (a), (b) Current-voltage characteristics of the single- and exciplex-host devices, respectively. (c), (d) EQE values.

reactions:



The steady state rate equations for the populations of charges and bright and dark triplets are constructed for a

given model from the following full expressions:

$$\begin{aligned} \frac{dT_B}{dt} = & -(k_{\text{rad}} + k_{B \rightarrow D} + k_{\text{sep}}^B)T_B \\ & + k_{D \rightarrow B}T_D + k_{\text{rec}}^B P^2 - k_{TTA}T_B^2 \\ & - k_{TTA}T_B T_D - k_{TPA}T_B P \end{aligned} \quad (\text{D1})$$

$$\begin{aligned} \frac{dT_D}{dt} = & k_{B \rightarrow D}T_B - (k_{D \rightarrow B} + k_{\text{sep}}^D)T_D \\ & + k_{\text{rec}}^D P^2 - k_{TTA}T_B T_D \\ & - k_{TTA}T_D^2 - k_{TPA}T_D P \end{aligned} \quad (\text{D2})$$

$$\begin{aligned} \frac{dP}{dt} = & 2k_{\text{rec}}^B T_B + 2k_{\text{rec}}^D T_D \\ & - (k_{\text{CL}} + k_{\text{sep}}^B + k_{\text{sep}}^D)P + J \end{aligned} \quad (\text{D3})$$

where the rate constants are defined above. The constant J in the polaron time derivative is the applied current density used to simulate electroluminescence experiments and is set to zero for photoluminescence. In this model, J is defined as the concentration of polarons injected per second such that its units of $\text{nm}^{-3} \text{s}^{-1}$ are a constant scaling factor away from the experimental units for current density.

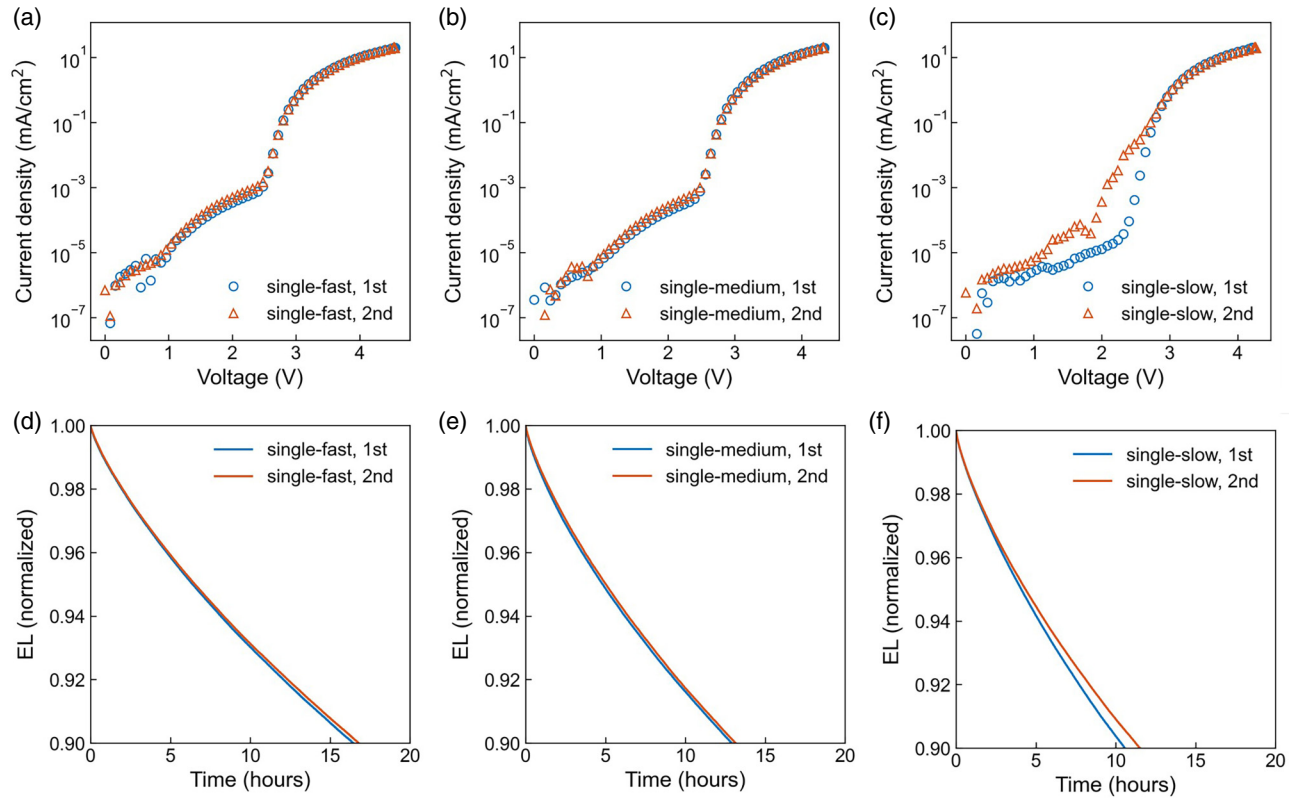


FIG. 11. (a)–(c) I - V characteristics comparing different devices fabricated with nominally identical processes. All OLEDs use a single-host material. The cathode used is (a) fast, (b) medium, and (c) slow. (d)–(f) Degradation characteristics for the devices shown in (a)–(c). Strong correlation between degradation rates and leakage current at low voltages is not observed.

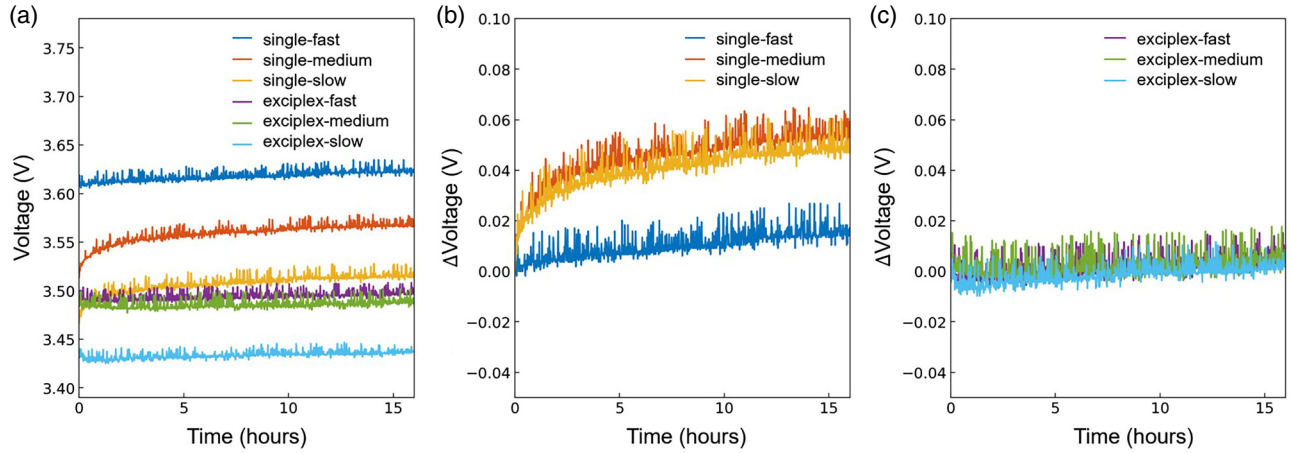


FIG. 12. (a) Operating voltage during OLED ageing experiments. The current density is maintained at $J = 5 \text{ mA/cm}^2$. Small differences are observed in the absolute voltages. (b) Trends in the voltage rise during device ageing are compared in single-host devices by normalizing at $t = 0$. The trends are identical within measurement error. (c) Trends in the voltage rise during device ageing are compared in exciplex host devices by normalizing at $t = 0$. The trends are identical within measurement error. The slopes for single-fast, single-medium, single-slow, exciplex-fast, exciplex-medium, and exciplex-slow are $7.3 \times 10^{-4} \text{ V/h}$, $1.3 \times 10^{-3} \text{ V/h}$, $1.2 \times 10^{-3} \text{ V/h}$, $4.7 \times 10^{-4} \text{ V/h}$, $3.1 \times 10^{-4} \text{ V/h}$, and $3.9 \times 10^{-4} \text{ V/h}$, respectively.

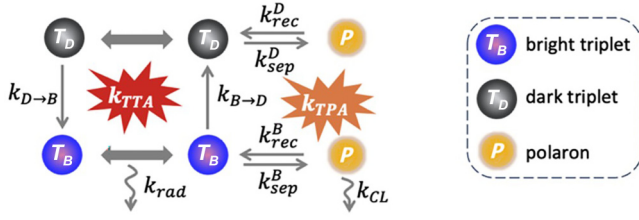


FIG. 13. Schematic of the kinetic processes considered in this theoretical modeling including their rate labels.

2. Photoluminescence simulation

The applied light intensity of a photoluminescence (PL) experiment is simulated by the following procedure:

1. Choose initial values for each rate constant included in the given model and initialize the population of bright triplets as nonzero. Set J equal to zero.
2. Use Eqs. (D1)–(D3) to evolve the populations of each species over the short PL time scale.
3. Use the normalized population of bright triplets at each time point to simulate the PL curve.

3. Electroluminescence simulation

From electroluminescence (EL) experiments, the external quantum efficiency (EQE) of a device can be calculated in this kinetic scheme as

$$\text{EQE} = \frac{\# \text{ photons emitted}}{\# \text{ charges injected}} = \frac{k_{\text{rad}} T_B^{(J)}}{J} \quad (\text{D4})$$

where J is the applied current density per second and $T_B^{(J)}$ is the steady state population of bright triplets under a given J . The process of modeling a roll-off curve is as follows.

1. Choose initial values for each rate constant included in the given model and initialize the populations of bright and dark triplets as nonzero.

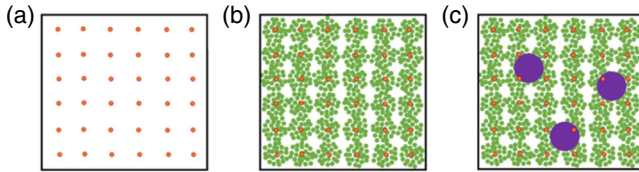


FIG. 14. Two-dimensional visualization of the parameter space built from the rates included in a given model and systematically searched in several steps, where (a) is a grid search of RMSE point calculations (orange dots), (b) is a local search (green dots) around each point in the grid search, and (c) is a thorough search (purple circles) of the regions with the best results determined in (b).

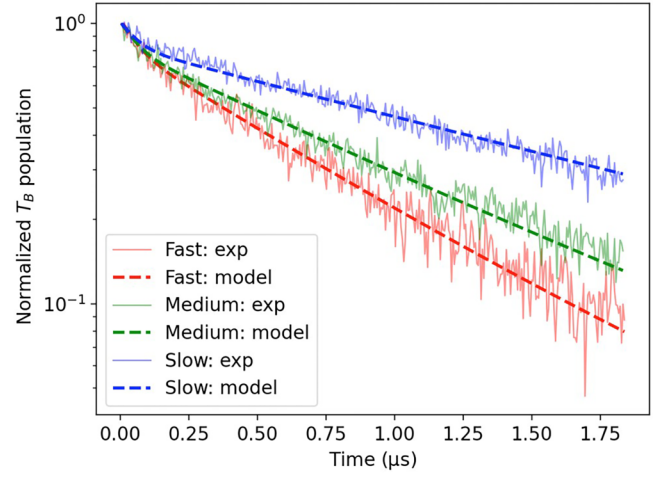


FIG. 15. Minimal model fit against experimental PL data for the single-host OLEDs with fast, medium, and slow coupling layers.

2. Set Eqs. (1)–(3) equal to zero and solve to reach the steady state populations of each species.
3. Calculate EQE using Eq. (D4).
4. Repeat Steps 2 and 3 for a range of applied current densities J .
5. Scale the calculated curve such that the maximum value is 100% EQE.

4. Fit to experimental data

To reproduce the experimental results for PL and EL experiments, we need to determine the optimal rate constants to use as parameters in a given model. To determine the relative quality of a set of parameters, we calculate the RMSE between our model and the experimental data.

To explore a variety of models we perform a thorough and systematic search of the parameter space composed of multiple rate constants whose values span up to 20 orders of magnitude. For each model, the resulting parameter space is searched on three different levels, as illustrated in Fig. 14.

1. A grid search of single-point RMSE calculations, as described in Appendices D.II and D.III, spanning the full parameter space. The set of optimizable rate constants in the given model is initialized with every permutation of $\{10^{-9}, 10^{-6}, 10^{-3}, 10^0, 10^3, 10^6, 10^9\}$.

2. A local search around each “good” grid point determined in Level 1 (the top 50% RMSE values), employing a Nelder-Mead optimization to minimize the RMSE between the model and the experimental data. For a PL fit, all rate constants in the model are considered parameters in the optimization. For an EL fit, the rate constants determined by the PL fit are held fixed, while all others are allowed to change.

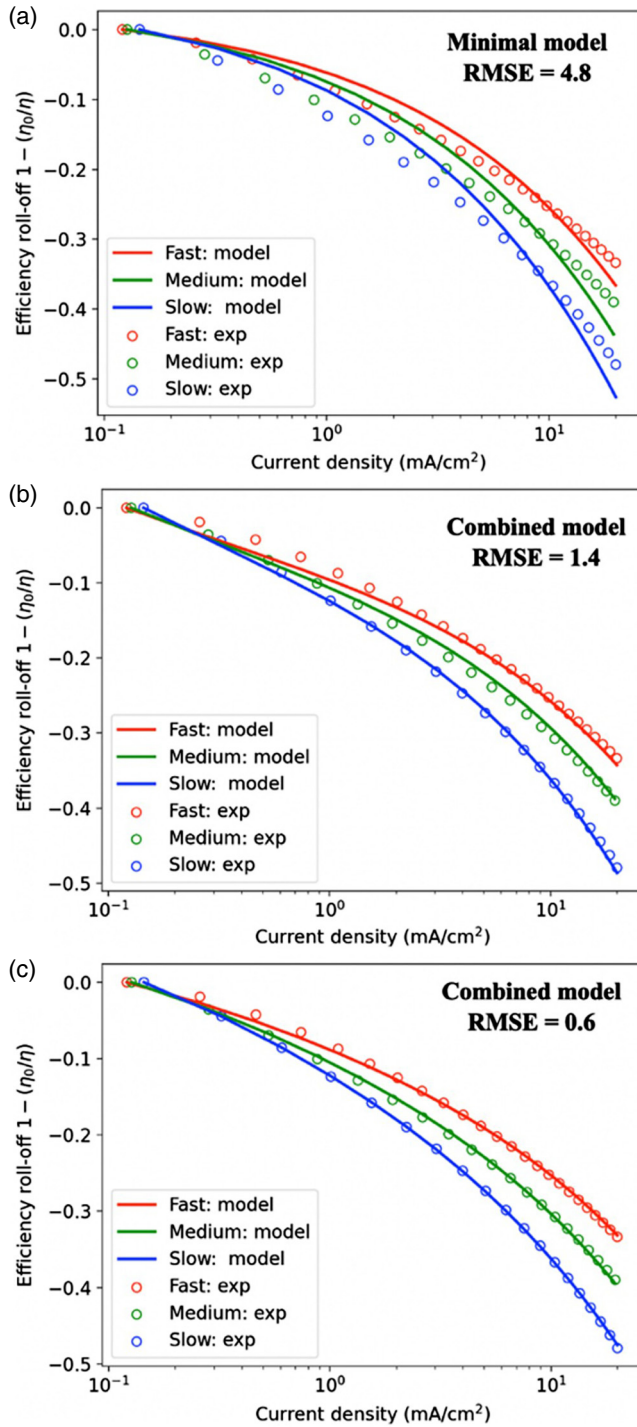


FIG. 16. Best results for the (a) minimal models, the (b) simplest combined models, and (c) fully combined models fitted against the experimental EL roll-off data for the single-host OLEDs with fast, medium, and slow coupling layers. The minimal model in (a) and fully combined model in (c) have coupling-layer-specific charge leakage rates.

3. A thorough scan of the regions with the best results from Levels 1 and 2 by perturbing the optimizable rate constants by every combination of $\{10^{-1}, 10^0, 10^1\}$.

The result of the parameter space search for a given set of rate constants is a large number of possible models, where RMSE values for a single OLED that are less than about 0.3 are considered to be a good fit to the experimental data.

APPENDIX E: KINETIC MODEL RESULTS

1. Computational setup

To constrain the models further for the given data sets, we group the OLEDs by host material, single host vs. exciplex host, such that there are three OLEDs included in each model. While many of the rate constants are model-wide, some are specific to the coupling layer (fast, medium, or slow) of the OLED. A total RMSE that is considered a good fit to the experimental data is therefore less than about one with roughly equal contributions from each OLED.

Many of the models include rate parameters that are not constrained by the experimental data, shown in parentheses in the following tables, especially in the combined models that offer a high degree of flexibility. While many of the rate parameters are consistently singular valued within the best results of a given model, some vary over many orders of magnitude without impacting the quality of the fit. Such rates are referred to as unconstrained by the experimental data. For each parameter in parentheses there is a model that has that rate well constrained, depending on which kinetic process is thought to be important while other processes do not influence the total RMSE.

With such flexible and often overfitted models, we make no conclusions about the resulting magnitudes of the rate parameters from one model to the next nor to values reported in the literature. Instead, the aim of this kinetic modeling is to determine if bright triplet processes are sufficient to reproduce the experimental data, or if the introduction of dark triplet processes is necessary to achieve well-fitting models.

2. Single-host OLEDs

In fitting the PL experimental data for the single-host OLEDs, a minimal model that includes only reactions involving bright triplets and charges was found to be a good fit with an RMSE of 0.09 [Table II(a)]. While the addition of reactions involving dark triplets to the minimal model provided slight improvement to the RMSE, the noise of the experimental data made those improvements ill-defined and led to overfitted models. While charge separation and recombination into bright triplets were both well described by universal rate constants, as seen in Table II(a), the bright triplet radiative decay rates are specific to the coupling layer of each OLED. Figure 15 shows the result of the PL fit using a minimal model.

Unlike for the PL, a minimal model with only bright triplets is not able to describe the shape of the roll-off curves for the single-host OLEDs. The best fit found after

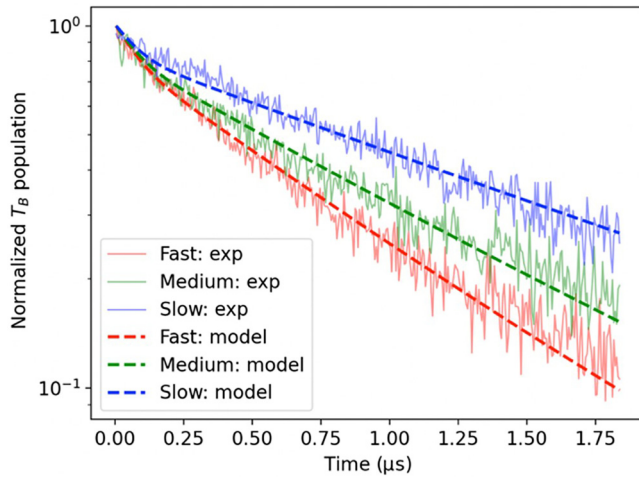


FIG. 17. Minimal model fit against experimental PL data for the exciplex host OLEDs with fast, medium, and slow coupling layers.

a thorough search of the parameter space and inclusion of coupling-layer-specific charge leakage parameters still has a total RMSE of well over one and is visually not a good fit to the experimental data [Fig. 16(a)]. However, as Table II(b) shows, when dark triplets are included in the model in any way, the fit improves significantly. Even the simplest dark triplet processes bring the RMSE down closer to one [Fig. 16(b)], but fitting the shape of the roll-off curves at low current density requires the addition of charge leakage to the model [Fig. 16(c)]. Both a universal charge leakage rate and coupling-layer-specific charge leakage rates bring the RMSE of the fit to one or less.

3. Exciplex-host OLEDs

In fitting the PL experimental data for the exciplex host OLEDs, a minimal model was again found to be a good fit with an RMSE of 0.10, and the addition of dark triplets did not improve the RMSE beyond the noise of the experimental model. The resulting rate constants of the PL fit using this minimal model are shown in Table III(a) and plotted in Fig. 17.

For the exciplex-host OLEDs, the experimental roll-off curves are fitted well using only a minimal model including reactions involving just charges and bright triplets. From Table III(b) we see that for this host, it is necessary to include coupling-layer-specific charge leakage rates to achieve a total RMSE of less than one. While the addition of dark triplets in various ways causes minor improvements to the total RMSE values, these improvements are significantly smaller than for the single-host OLEDs, and visually in Fig. 18 there is little difference between the minimal and combined models.

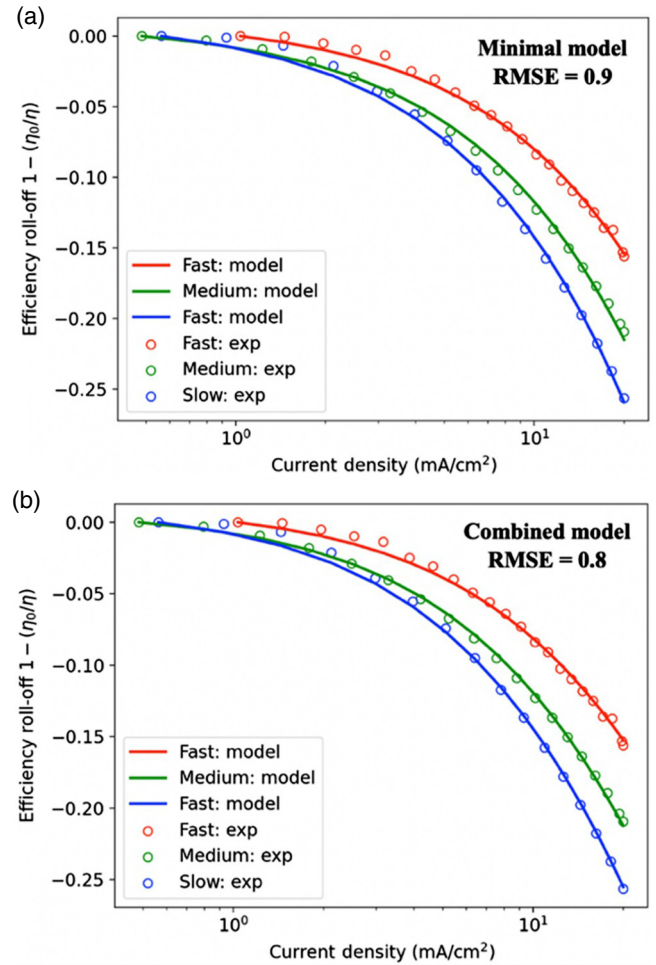


FIG. 18. Best results for the (a) minimal and (b) combined models fit against the experimental EL roll-off data for the exciplex host OLEDs with fast, medium, and slow coupling layers. Both models shown have coupling-layer-specific charge leakage rates.

4. Model validation

The kinetic modeling setup is entirely dependent on fitting to experimental data. Where there is any potential ambiguity as to which experimental data points to include in the fitting process, it is important to explore how those assumptions impact the results of the modeling. In this section we work through the effect of truncating first the PL data set and then the EL, repeating the modeling performed in the previous sections for each scenario.

a. Truncated photoluminescence data

There is some ambiguity as to where the “real” PL experimental data that is fully representative of the devices begins and ends. Therefore, we explore the effect on the theoretical modeling when the short- and long-time PL data are excluded from the modeling. Using just the middle third of the PL data requires only linear fits, making

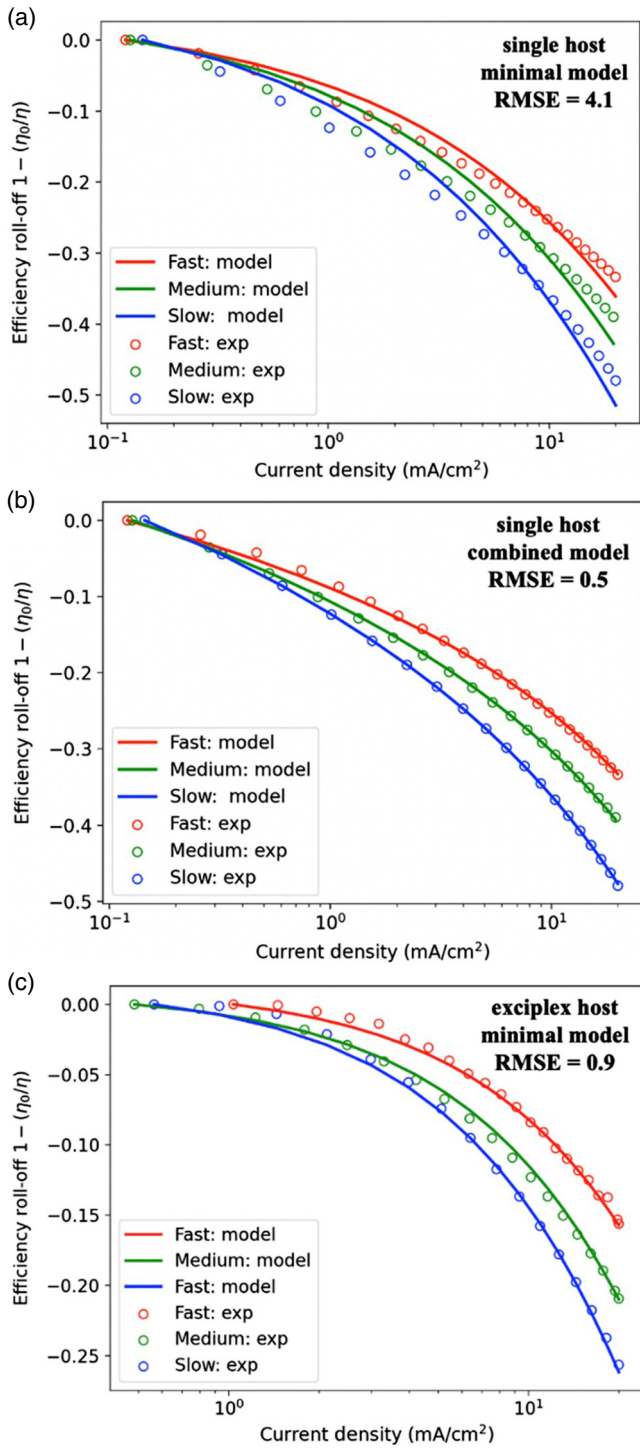


FIG. 19. Best results for the (a), (c) minimal and (b) combined models fitted against the experimental EL roll-off data for the (a), (b) single and (c) exciplex host OLEDs using radiative rates fitted to the truncated PL experimental data. All models use coupling-layer-specific charge leakage rates.

all bimolecular rates, like charge separation and recombination, unnecessary and instead included in the fit to the experimental roll-off data. Despite the additional flexibility

in the roll-off models, the same quality of fits for both types of host material are achieved as in the full model and lead to the same overall results. The single-host models require the addition of dark triplet processes and charge leakage to achieve a well-fitting model [Figs. 19(a) and 19(b)], and a minimal model including charge leakage is sufficient to achieve a good fit to the experimental data of the exciplex host OLEDs [Fig. 19(c)].

b. Truncated roll-off data

The experimental EQE data at low current densities are impacted by processes such as charge leakage. The roll-off data points included in the full model in Appendix E are chosen to begin at the maximum EQE value. To explore the effect of charge leakage in the theoretical models, we truncate the roll-off data by removing the data points at the lowest two current densities for all devices. Using the same PL fits as in Appendix E, the shortened roll-off curves are re-fitted. Exclusion of the roll-off data points at low current density eliminates the dependence on charge leakage rates to achieve a good fit for the single-host OLEDs (Fig. 20), while it has no effect on models of the exciplex devices, where charge leakage remains a necessary process (Fig. 21). Aside from the charge leakage rate, the overall results for both the single- and exciplex-host OLEDs are the same as presented in the full model.

5. Modeling conclusions

Using a kinetic scheme that considers polarons, bright triplets, and dark triplets, we define a “minimal” model that includes only the processes that govern polarons and bright triplets and a “combined” model that adds those of dark triplets as well as interconversion between bright and dark. The PL experimental data for both the single-host and exciplex-host OLEDs are well fitted using a minimal model of charge separation and recombination as well as radiative rates specific to each coupling layer.

Keeping these PL-determined rates fixed, fitting to the roll-off curves of each device resulted in many well-fitting yet highly flexible and underdetermined models. Some rates are constrained by the experimental data, while others ranged over many orders of magnitude with no effect on the quality of the fit. Despite the high degree of flexibility, however, the single-host roll-off curves could not be well fitted using any version of the minimal model. Instead, the introduction of dark triplet processes with the combined model was necessary to recreate the correct curve shape. In contrast, the roll-off curves for the exciplex host devices required only a minimal model and no additional dark triplet rates to achieve a good fit. This remains true even when we consider subsets of the experimental data, as described in Appendix E.IV.

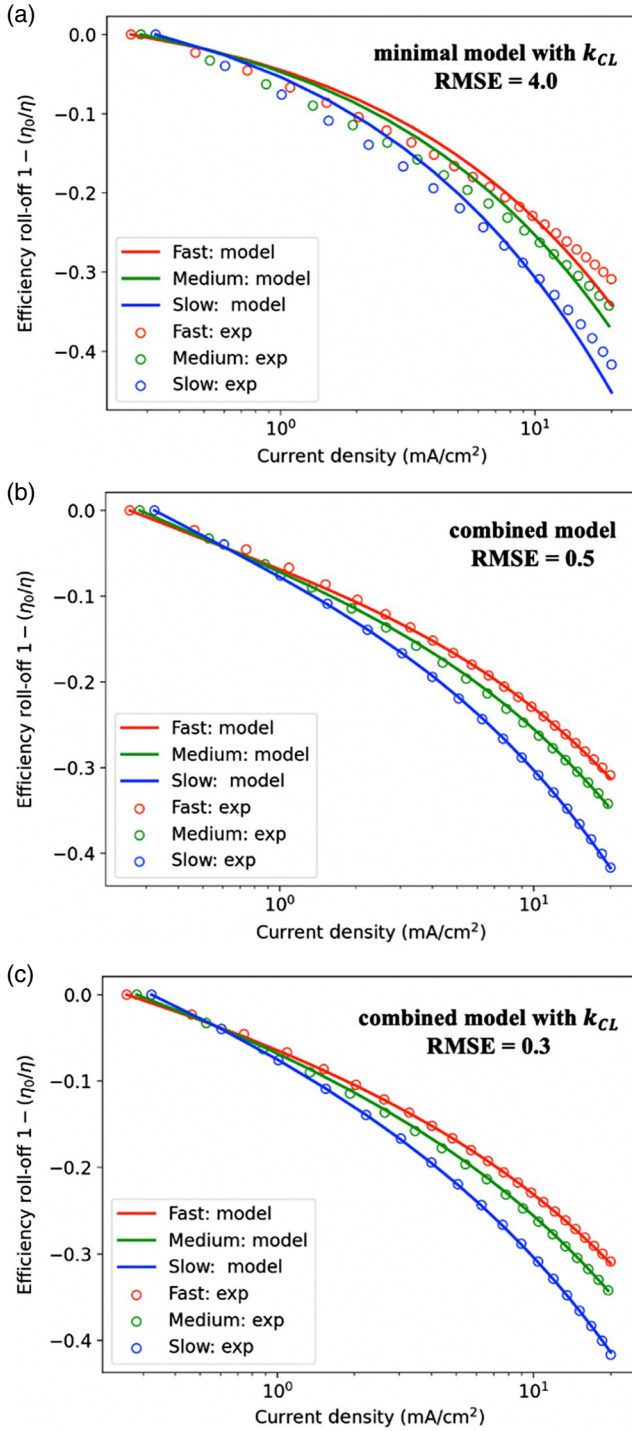


FIG. 20. Best results for the (a) minimal, (b) combined models without charge leakage and (c) combined models with charge leakage. All models fit against the truncated experimental EL roll-off data for the single-host OLEDs with fast, medium, and slow coupling layers.

We conclude that dark triplet processes are important for describing the experimental PL and roll-off data of the single-host OLEDs whereas they are unnecessary for the exciplex host OLEDs.

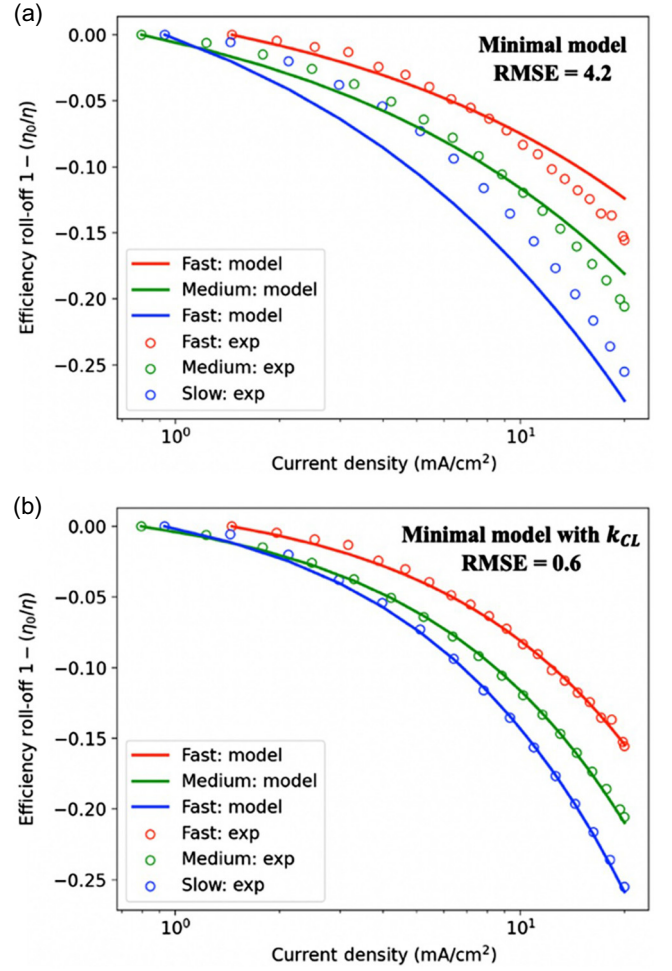


FIG. 21. Best result for the minimal models (a) without charge leakage and (b) with coupling-layer-specific charge leakage rates. All models fit against the truncated experimental EL roll-off data for the exciplex host OLEDs with fast, medium, and slow coupling layers.

APPENDIX F: MEAM MODEL AND DATA FITTING

1. Extended Merrifield model of triplet-triplet annihilation

To interpret the MEAM data, an extension of the Merrifield model of TTA is developed here and of TPA in Appendix F.II. The spin pair Hamiltonian, which describes both the zero-field splitting of dark triplets as well as how two triplets interact, is given by

$$\begin{aligned}
 \hat{H}_{\text{spin}} = & g\mu_B \vec{B} \cdot (\hat{S}_1 + \hat{S}_2) + D_1 \left(\hat{S}_{z1}^2 - \frac{1}{3} \hat{S}_1^2 \right) \\
 & + E_1 (\hat{S}_{x1}^2 - \hat{S}_{y1}^2) + E_1 (\hat{S}_{x1}^2 - \hat{S}_{y1}^2) \\
 & + R \left[D_2 \left(\hat{S}_{z2}^2 - \frac{1}{3} \hat{S}_2^2 \right) + E_2 (\hat{S}_{x2}^2 - \hat{S}_{y2}^2) \right] R^{-1} \\
 & + J (\hat{S}_{x1} \cdot \hat{S}_{x2} + \hat{S}_{y1} \cdot \hat{S}_{y2} + \hat{S}_{z1} \cdot \hat{S}_{z2}) \quad (\text{F1})
 \end{aligned}$$

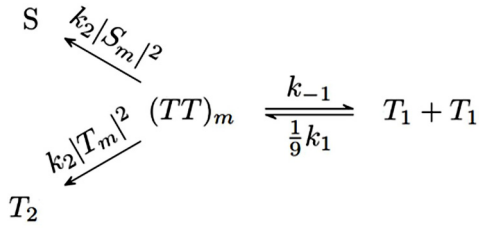


FIG. 22. Simplified kinetic model of dark triplet TTA, where dark triplets (T_D) form pair states that may populate a hot singlet (S) or hot triplet (T_D) state.

as was utilized by Piland *et al.* [31] and later clarified by Tapping *et al.* [32], where

$$R = e^{-\frac{i}{\hbar}(\gamma\hat{S}_{x2} + \beta\hat{S}_{y2} + \alpha\hat{S}_{z2})} \quad (\text{F2})$$

$$\vec{B} = B \begin{pmatrix} \sin(\theta) \cos(\varphi) \\ \sin(\theta) \sin(\varphi) \\ \cos(\varphi) \end{pmatrix} \quad (\text{F3})$$

encodes the orientation of triplet 1 with respect to triplet 2 and the external magnetic field. This Hamiltonian was then applied to a simplified kinetic scheme of dark triplet TTA, where either a hot singlet or triplet state on the host may be populated through TTA between dark triplets (Fig. 22).

Under steady-state conditions, the simplified model yields the effective singlet and triplet TTA rate constants to S and T_D given by

$$k_{S-TTA}^D \left(B, \frac{k_{-1}}{k_2}, \alpha, \beta, \gamma, \theta, \varphi \right) = \frac{1}{9} k_1 \sum_m \frac{|S_m|^2}{\frac{k_{-1}}{k_2} + |S_m|^2 + |T_m|^2} \quad (\text{F4})$$

$$k_{T-TTA}^D \left(B, \frac{k_{-1}}{k_2}, \alpha, \beta, \gamma, \theta, \varphi \right) = \frac{1}{9} k_1 \sum_m \frac{|T_m|^2}{\frac{k_{-1}}{k_2} + |S_m|^2 + |T_m|^2} \quad (\text{F5})$$

which depend on the branching ratio of triplet pair dissociation to fusion (k_{-1}/k_2), as well as the total singlet ($|S_m|^2$) and triplet ($|T_m|^2$) character of each triplet pair state m . The singlet and triplet character of the pairs is given by the eigenstates of the spin pair Hamiltonian, which depend on the applied field, zero-field splitting, interaction angle, and exchange coupling. Assuming amorphous host deposition, we expect interacting dark triplets to be randomly oriented with respect to one another and the externally applied magnetic field. To average over all possible interaction and

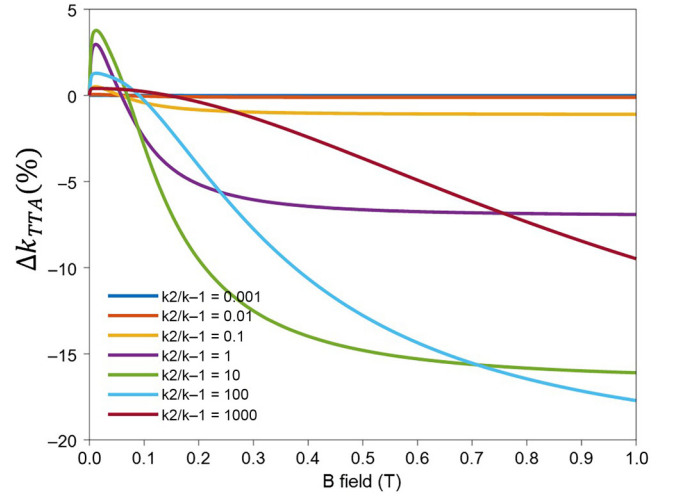


FIG. 23. Total TTA MEAM responses as a function of applied magnetic field magnitude. The TTA MEAM curve always has a characteristic peak and then decline, but changes in shape depending on the k_{-1}/k_2 branching ratio.

field angles, a left-Riemann sum was used over the interaction angles α , β , and γ , as well as the field angles θ and φ :

$$k_{TTA}^D \left(B, \frac{k_{-1}}{k_2} \right) \approx \frac{1}{32\pi^3} \sum_0^{2\pi-\Delta\alpha} \sum_0^{\pi-\Delta\beta} \sum_0^{2\pi-\Delta\gamma} \sum_0^{2\pi-\Delta\theta} \sum_0^{\pi-\Delta\varphi} \cdot k_{TTA}^D \left(B, \frac{k_{-1}}{k_2}, \alpha, \beta, \gamma, \theta, \varphi \right) \cdot \sin(\beta) \sin(\varphi) \Delta\varphi \Delta\theta \Delta\gamma \Delta\beta \Delta\alpha \quad (\text{F6})$$

From this integral we generate a set of total TTA rate constant MEAM curves (Fig. 23) defined as

$$\Delta k_{TTA}^D \left(\frac{k_{-1}}{k_2} \right) = \frac{k_{S-TTA}^D \left(B, \frac{k_{-1}}{k_2} \right) + k_{T-TTA}^D \left(B, \frac{k_{-1}}{k_2} \right)}{k_{S-TTA}^D \left(0, \frac{k_{-1}}{k_2} \right) + k_{T-TTA}^D \left(0, \frac{k_{-1}}{k_2} \right)} - 1 \quad (\text{F7})$$

Total TTA rate constant MEAM parameters and responses are shown in Table IV and Fig. 23, respectively.

2. Extended Merrifield model of triplet-polaron annihilation

Similar to the case of TTA, we can define the spin pair Hamiltonian for a triplet-doublet (polaron) pair as

$$\hat{H}_{\text{spin}} = g\mu_B \vec{B} \cdot (\hat{S}_T + \hat{S}_D) + D \left(\hat{S}_{zT}^2 - \frac{1}{3} \hat{S}_T^2 \right) + E (\hat{S}_{xT}^2 - \hat{S}_{yT}^2) + J (\hat{S}_{xT} \cdot \hat{S}_{xD} + \hat{S}_{yT} \cdot \hat{S}_{yD} + \hat{S}_{zT} \cdot \hat{S}_{zD}) \quad (\text{F8})$$

TABLE IV. Total TTA rate constant MEAM parameters. Small (μeV) zero field splittings were used to represent the dark triplets, and a small (neV) exchange coupling was used as weak field strengths modify only the weakly exchange coupled triplet pair dynamics [31].

$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$	$\Delta\theta$	$\Delta\phi$	J	D_1, D_2	E_1, E_2	k_2/k_{-1}
$\frac{\pi}{6}$	$\frac{\pi}{6}$	$\frac{\pi}{6}$	$\frac{\pi}{6}$	$\frac{\pi}{6}$	-1 neV	$8.6 \mu\text{eV}$	$-1.7 \mu\text{eV}$	$[0.001-1000]$

where there is no zero-field splitting of the polaron. In TPA, a dark triplet and a polaron form coupled pair states that may form a hot polaron. The simplified kinetic model of TPA, which involves the formation of these pair states, is given in Fig. 24.

Under steady-state conditions, the model yields an effective rate constant for the formation of hot polarons given by

$$k_{\text{TPA}}^D \left(B, \frac{k_{-1}}{k_2}, \theta, \varphi \right) = \frac{1}{6} k_1 \sum_m \frac{|D_m|^2}{(k_{-1}/k_2) + |D_m|^2} \quad (\text{F9})$$

Since polarons lack zero-field splitting, there is no effect of triplet orientation on the TPA MEAM curve. The orientation of the external field will still change the MEAM curve, so we average over all field orientations using a left-Riemann sum given by

$$k_{\text{TPA}}^D \left(B, \frac{k_{-1}}{k_2} \right) \approx \frac{1}{4\pi} \sum_0^{2\pi-\Delta\theta} \sum_0^{\pi-\Delta\varphi} k_{\text{TPA}}^D \left(B, \frac{k_{-1}}{k_2}, \theta, \varphi \right) \cdot \sin(\varphi) \Delta\varphi \Delta\theta \quad (\text{F10})$$

From this integral we generate a set of TPA MEAM curves (Fig. 25) defined by

$$\Delta k_{\text{TPA}}^D \left(\frac{k_{-1}}{k_2} \right) = \frac{k_{\text{TPA}}^D(B, (k_{-1}/k_2))}{k_{\text{TPA}}^D(0, (k_{-1}/k_2))} - 1 \quad (\text{F11})$$

Total TPA rate constant MEAM parameters and response curve are shown in Table V and Fig. 25, respectively.

III. Electroluminescence magnetic exciton annihilation modulation curve fitting

To relate the MEAM responses of the TTA and TPA rates in dark triplets to the observed electroluminescence

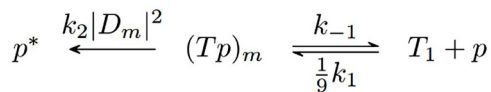


FIG. 24. Simplified kinetic model of TPA, where dark triplets (T_D) and band edge polarons (P) interact to form highly excited hot polarons that quickly relax to the band edge.

quantum efficiency, the following equation of motion from Reineke *et al.* [33] for dark triplets in the host was applied, which considers only interactions involving dark triplets, as these are the only rates which will be changed under weak (0–0.5 T) magnetic fields:

$$\frac{dT_D}{dt} = \frac{3}{4} k_G - \frac{1}{\tau} T_D - (k_{S-TTA}^D + k_{T-TTA}^D) T_D^2 - k_{\text{TPA}}^D T_D P \quad (\text{F12})$$

which under steady state conditions yields the electroluminescence efficiency

$$\eta_{\text{EL}} \left(B, \frac{k_{-1}}{k_2} \right) = \frac{3}{4} \cdot \frac{k_r}{(1/\tau) + (k_{S-TTA}^D + k_{T-TTA}^D) T_D^2 + k_{\text{TPA}}^D T_D P} + \frac{1}{4} \eta_s \quad (\text{F13})$$

The effects of rate constant and population in the TTA and TPA rates are combined, such that the electroluminescence

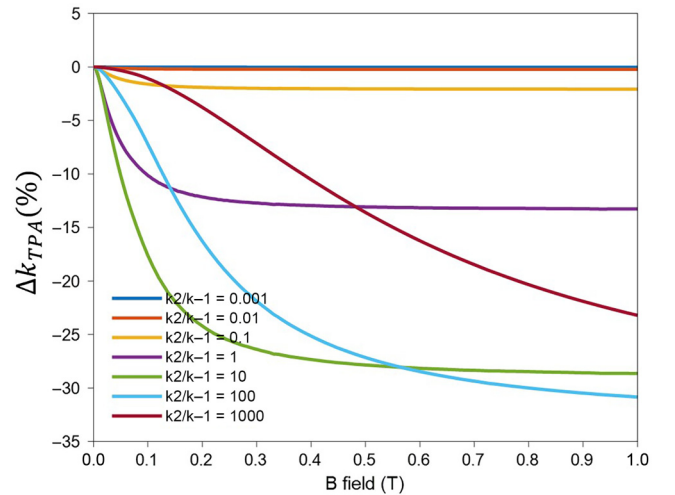


FIG. 25. Total TPA MEAM response curves as a function of magnetic field magnitude. The TPA rate always monotonically decreases as a function of field strength, but its curvature is modulated by the k_2/k_{-1} branching ratio.

TABLE V. Total TPA rate constant MEAM parameters. Small (μeV) zero field splittings were used to represent the dark triplets, and a small (neV) exchange coupling was used as weak field strengths modify only the weakly exchange coupled triplet-polaron pair dynamics.

$\Delta\theta$	$\Delta\phi$	J	D	E	k_2/k_{-1}
$\frac{\pi}{67}$	$\frac{\pi}{67}$	-1 neV	$8.6 \mu\text{eV}$	$-1.7 \mu\text{eV}$	$[0.001\text{--}1000]$

efficiency depends on the overall rates (Γ) of each process:

$$\eta_{\text{EL}} \left(B, \frac{k_{-1}}{k_2} \right) = \frac{3}{4} \cdot \frac{k_r}{\frac{1}{\tau} + \Gamma_{\text{TTA}} \left(B, \frac{k_{-1}}{k_2} \right) + \Gamma_{\text{TPA}} \left(B, \frac{k_{-1}}{k_2} \right)} + \frac{1}{4} \eta_S \quad (\text{F14})$$

From this expression, the electroluminescence MEAM curve was defined as

$$\Delta\eta_{\text{EL}} \left(\frac{k_{-1}}{k_2} \right) = \alpha \left[\frac{\eta_{\text{EL}}(B, (k_{-1}/k_2))}{\eta_{\text{EL}}(0, (k_{-1}/k_2))} - 1 \right] \quad (\text{F15})$$

where a long dark triplet lifetime and an η_S of 0.8 are assumed. The coarse-grained parameter ($0 < \alpha < 1$) is used to vertically scale the predicted MEAM curve to the measured data, as there are other sources of electroluminescence such as bright triplets that dilute the MEAM of dark triplet annihilation events. The resultant fits are provided in Fig. 5 in the main text. To generate these fits, the parameter space in Table VI was explored.

The best fit to the data was determined through least-squares optimization of every combination in the parameter space, resulting in the values in Table VII.

APPENDIX G: DERIVATION OF THEORETICAL EXPECTATIONS FOR OLED ROLL-OFF DEPENDENCE ON TRIPLET LIFETIME

To derive theoretical expectations for the dependence of roll-off on bright triplet exciton lifetime caused by TPA and TTA events with bright triplets, we adopt a rate equations model as used by Reineke *et al.* [33]. Defining the rate equations for triplet density, the model takes the following form:

$$\frac{dT_B}{dt} = \frac{j}{e w_{\text{rec}}} - \frac{T}{\tau} - \frac{1}{2} k_{\text{TTA}} T_B^2 - \frac{k_{\text{TPA}} \rho(j)}{e} T_B \quad (\text{G1})$$

TABLE VI. Parameter space used for electroluminescent MEAM fits.

D	E	k_2/k_{-1}	$\Gamma_{\text{TTA}}/\Gamma_{\text{TPA}}$	α
$[0.1:0.1:20] \times 8.6 \mu\text{eV}$	$-[0.1:0.1:20] \times 1.7 \mu\text{eV}$	$[0.001\text{--}1000]$	$[0.001\text{--}1000]$	$[0.01:0.01:1]$

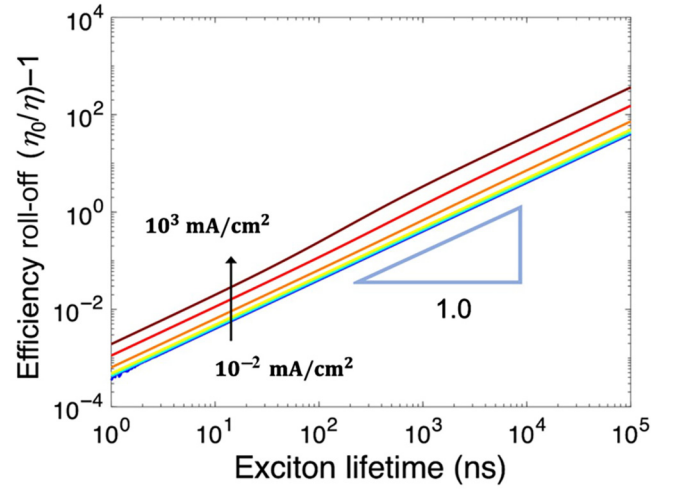


FIG. 26. Theoretical derivations for roll-off expressed as $-\Delta\eta_{\text{EL}} = (\eta(0)/\eta(j)) - 1$ showing an approximately linear power law dependence on exciton lifetime for all current densities.

where j is the current density, e is the elementary charge, w_{rec} is the recombination zone width, τ is the triplet exciton lifetime as measured by transient photoluminescence, $\rho(j)/e$ is the charge carrier density in the recombination zone at a given current density, and k_{TT} and k_{TP} are the rate constants associated with TTA and TPA, respectively.

We can isolate the current-density-dependent losses in efficiency by defining the efficiency roll-off $\Delta\eta_{\text{EL}}$ relative to the efficiency limit at $j = 0$, $\eta_{\text{EL}}(0)$ [9]:

$$\Delta\eta_{\text{EL}} = 1 - \frac{\eta_{\text{EL}}(0)}{\eta_{\text{EL}}(j)} \quad (\text{G2})$$

Modeling both triplet-polaron and triplet-triplet annihilation using the rate equation described in Eq. (G1) yields

$$\Delta\eta_{\text{EL}} = \frac{1}{2} - \frac{\tau k_{\text{TPA}} \rho(j)}{2e} - \frac{1}{2} \sqrt{\left(1 + \frac{\tau k_{\text{TPA}} \rho(j)}{e} \right)^2 + \frac{2k_{\text{TTA}} j \tau^2}{e w_{\text{rec}}}} \quad (\text{G3})$$

Which in the limit of $(\tau k_{\text{TPA}} \rho(j))/e \gg 1$ can be simplified as

$$\Delta\eta_{\text{EL}} = \frac{1}{2} - \tau k_{\text{loss}}(j) \quad (\text{G4})$$

Indicating that at long lifetimes, high currents, or fast TPA efficiency roll-off scales linearly with exciton lifetime.

TABLE VII. Best fits of electroluminescent MEAM curves in Fig. 5.

Device	D	E	k_2/k_{-1}	$\Gamma_{\text{TTA}}/\Gamma_{\text{TPA}}$	α
Single fast	43.86 μeV	$-8.772 \mu\text{eV}$	0.1	0.501	0.44
Exciplex fast	13.76 μeV	$-2.752 \mu\text{eV}$	0.01	0.001	0.14
Single slow	53.32 μeV	$-10.66 \mu\text{eV}$	3	0.063	0.29
Exciplex slow	3.44 μeV	$-0.688 \mu\text{eV}$	5	0.000	0.15

From Reineke *et al.* [33] we estimate the charge density in a space-charge limited current model as follows:

$$\rho \approx \frac{V_{\text{appl}}(j)\epsilon_r\epsilon_0}{d^2} \quad (\text{G5})$$

where ϵ_0 and ϵ_r are the vacuum permittivity and the OLED's relative permittivity, respectively. d is the width of the EML, and $V_{\text{appl}}(j)$ is the voltage applied to the for any given current density.

We insert representative values for all constants, $k_{\text{TTA}} = 10^{-18} \text{ m}^3 \text{ s}^{-1}$ and $k_{\text{TPA}} = 10^{-19} \text{ m}^3 \text{ s}^{-1}$ [33], $\epsilon_r = 2.9$ (assuming an organic refractive index of $n = 1.7$), $d = 10 \text{ nm}$ for the devices fabricated here, and an estimated $w_{\text{rec}} \approx 5 \text{ nm}$.

In Fig. 26, we plot efficiency roll-off expressed as $-\Delta\eta_{\text{EL}} = \frac{\eta(0)}{\eta(j)} - 1$ for values of j ranging from $10^{-2} \text{ mA cm}^{-2}$ to 10^3 mA cm^{-2} . The corresponding voltages are determined from the current-voltage characteristics: $V_{\text{appl}} \approx 2.7 \text{ V}$ ($10^{-2} \text{ mA cm}^{-2}$), 2.85 V ($10^{-1} \text{ mA cm}^{-2}$), 3 V (10^0 mA cm^{-2}), 4 V (10^1 mA cm^{-2}), 7 V (10^2 mA cm^{-2}), 12 V (10^3 mA cm^{-2}). As shown in Fig. 26, the expected slope for the dependence of roll-off as $\eta(0)/\eta(j) - 1$ on triplet lifetime, τ , is approximately 1 for all current densities.

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