

Interfacial Exciton-Polaron Quenching in Organic Light-Emitting Diodes

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In organic light-emitting diodes (OLEDs), understanding the efficiency loss mechanism known as exciton-polaron quenching (EPQ) has been a longstanding challenge. Traditionally, EPQ was believed to occur mainly *within* the bulk of the OLED emission layer (EML) due to the coexistence of polarons and excitons, limiting our understanding of its full impact. Here, we report a previously overlooked phenomenon termed “interfacial EPQ (Inf. EPQ),” which occurs at the heterointerface between the EML and the adjacent charge transport layer (CTL). We observe the *direct* transfer of EML excitons to CTL polarons across this interface, spanning distances of up to 4 nm. Notably, Inf. EPQ exceeds EPQ within the EML bulk, even in devices with a *slight* interfacial energy barrier (> 0.2 eV). We propose a methodology that enables independent probing of Inf. EPQ, systematic validation of its essential parameters, and the identification of Dexter energy transfer as its governing mechanism. Importantly, our findings highlight Inf. EPQ as a *ubiquitous* phenomenon across devices with various luminescent mechanisms, wavelengths, and injection levels. By effectively addressing Inf. EPQ, we achieve efficiency enhancements in red, green, and blue phosphorescent OLEDs, by $70\% \pm 8\%$, $47\% \pm 5\%$, and $66\% \pm 6\%$, respectively. Our work advances the physical understanding of exciton and polaron dynamics at organic heterointerfaces, providing *universally* applicable solutions to Inf. EPQ-related issues in practical devices.

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I. INTRODUCTION

Organic light-emitting diodes (OLEDs) have advanced display technology across a wide range of applications, from smartphones and televisions to tablets, wearables, and automotive displays [1]. These OLED applications are renowned for their decent luminescent efficiency [2–6], vibrant color rendering [7,8], adaptable free-form designs [9–11], profound high-dynamic-range expression [12,13], and customizable viewing angle [14]. These features stem from the distinct electrical, optical, and mechanical characteristics of the organic semiconductors constituting OLEDs [15].

Among these features of OLEDs, achieving nearly 100% internal quantum efficiency (IQE) is crucial, which is accomplished by employing phosphorescent [16,17] and thermally activated delayed fluorescent (TADF) dopants [18,19] within the OLED emission layer (EML). To push such OLEDs towards their IQE limit, optimizing exciton generation and minimizing their loss are essential. This need necessitates precise control of polarons—the source of excitons—to ensure their efficient and balanced transport, injection, and confinement within the EML while mitigating their involvement in exciton-loss mechanisms [20,21].

However, most OLEDs face the challenge of polaron accumulation and resultant exciton-polaron quenching (EPQ) due to an inherent energy-level mismatch between the electrode’s work function and the frontier orbitals of the EML molecules, typically ranging from 1 to 2 eV [22]. Modern OLED architecture addresses this challenge by incorporating multiple charge transport layers (CTLs) to establish cascading energy-level alignment, facilitating polaron injection from the electrode into the EML.

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Nonetheless, blue OLEDs, with an EML energy gap exceeding that of their red and green counterparts by at least 0.4 eV, encounter difficulties in eliminating energy barriers at the CTL/EML interface. Solution-processed devices are no exception due to their limited multilayer configuration [23].

Polaron accumulation, particularly at the CTL/EML interface, diminishes not only the conductivity [24] but also the efficiency [25,26] and operational lifetime [27–29] of OLEDs. Despite its detrimental yet ubiquitous nature, surprisingly few studies have addressed polaron accumulation, although its extent is comparable to or even greater than what is found *within* the EML [30], provoking significant EPQ across the heterointerface under various conditions. For example, Kakumachi *et al.* reported exciton quenching by positive polarons accumulated at the interface. However, the phenomenon was limited to blue fluorescent OLEDs at low injection levels ($< 1 \text{ mA cm}^{-2}$), without disclosing the detailed extent and governing mechanisms [31]. Ferschke *et al.* detected a similar phenomenon when bilayer fluorescent devices were subjected to reverse bias voltages, which represent an impractical regime in terms of device operation [32].

The major difficulty arises from the lack of a proper methodology to distinguish exciton loss caused by interfacial polarons from the overall processes involving polarons and excitons, universally applicable to OLEDs of various types under diverse operating conditions. In this study, we define the phenomenon as “interfacial exciton-polaron quenching (Inf. EPQ),” involving remote and direct energy transfer of EML excitons to CTL polarons across the heterointerface. We propose a method and device architecture tailored for directly probing this Inf. EPQ, overcoming challenges faced by previous works. Our approach allows us to systematically vary and identify key determining factors of Inf. EPQ, revealing its universal occurrence across (i) diverse luminescent mechanisms, (ii) wavelengths, and (iii) injection levels.

For our experiments, we designed a series of bilayer organic hole-only devices (HODs), consisting of a hole-transport layer (HTL) and an EML. We modulated the accumulation of positive polarons at the HTL/EML interface by adjusting the energy-level offset (ΔE) between the highest occupied molecular orbitals (HOMOs) of the chosen HTL and EML. We systematically varied the physical separation of excitons from the accumulated polarons by introducing a thin emissive doped layer within the EML at varying distances (L) from the HTL/EML interface. Here, excitons were exclusively generated within the doped layer via laser illumination, absorbable *only* by the dopant.

Our findings provide two pieces of evidence confirming the presence of Inf. EPQ. First, a large ΔE more significantly attenuates the steady-state photoluminescence (PL) intensity from the dopant, as current density (J) applied to the HODs increases across a range from 10^{-4} up to 10^2 mA cm^{-2} . This behavior is attributed to the enhanced

polaron accumulation at the HTL/EML interface with increasing J and ΔE , triggering significant Inf. EPQ. Second, the doped layer present within $L \lesssim 4 \text{ nm}$ activates Inf. EPQ, leading to a notable reduction in PL intensity. This observation suggests that Inf. EPQ can be intensified by a decreased exciton-polaron separation (L) across the heterointerface. By examining the trend of PL vs J characteristics relative to L , we identify Dexter energy transfer (DET) as a governing mechanism of Inf. EPQ.

Another significant discovery pertains to the universal occurrence of Inf. EPQ in HODs with diverse dopant PL mechanisms, including phosphorescence, fluorescence, or TADF. The extent of PL reduction is closely linked to the effective decay time of the excitons governing each PL mechanism. Based on our understanding, we demonstrated that the external quantum efficiencies (EQEs) of red, green, and blue phosphorescent OLEDs (PHOLEDs) can be enhanced by $70\% \pm 8\%$, $47\% \pm 5\%$, and $66\% \pm 6\%$, respectively, through the effective minimization of ΔE , establishing it as a general strategy to mitigate Inf. EPQ and thus achieve the utmost attainable efficiency. Our study not only advances the understanding of physical aspects of Inf. EPQ but also paves the way for practical engineering solutions to issues involving Inf. EPQ.

II. EXPERIMENT

Figure 1(a) shows the configuration of bilayer HODs, comprising a 100-nm aluminum (Al) anode, a hole injection layer (HIL) consisting of 10-nm MoO_3 and 3-nm 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CBP), a 50-nm HTL, a 50-nm EML with a 1-nm-thick doped layer inserted at varying distances (L) from the HTL/EML interface, and a 10-nm MoO_3 and 70-nm indium tin oxide (ITO) cathode. The incorporation of the CBP interlayer within the HIL effectively reduces the polaron injection barrier by forming an Ohmic-like contact between the anode and HTL [33,34]. This design eliminates undesirable injection-limited artifacts in bulk transport behaviors in HODs, allowing us to focus mainly on Inf. EPQ (see the Supplemental Material [35], Sec. 1).

The HODs were exposed to a 442-nm HeCd continuous-wave laser (Kimmon) with an intensity of 17 mW/cm^2 , exclusively generating excitons within the doped layer at L , while other layers remained optically inactive (see the Supplemental Material [35], Sec. 2, for the absorption spectra of all materials used). This approach effectively circumvents complexities arising from exciton energy transfer from the host to the dopant or exciton-exciton annihilations between the two, enabling precise control over dopant exciton generation—a key to analytically investigating Inf. EPQ.

Along with laser illumination, we varied the level of current density (J) applied to the HODs using a source-measure unit (2604b, Keithley) to modulate polaron accumulation at the HTL/EML interface, and consequential Inf.

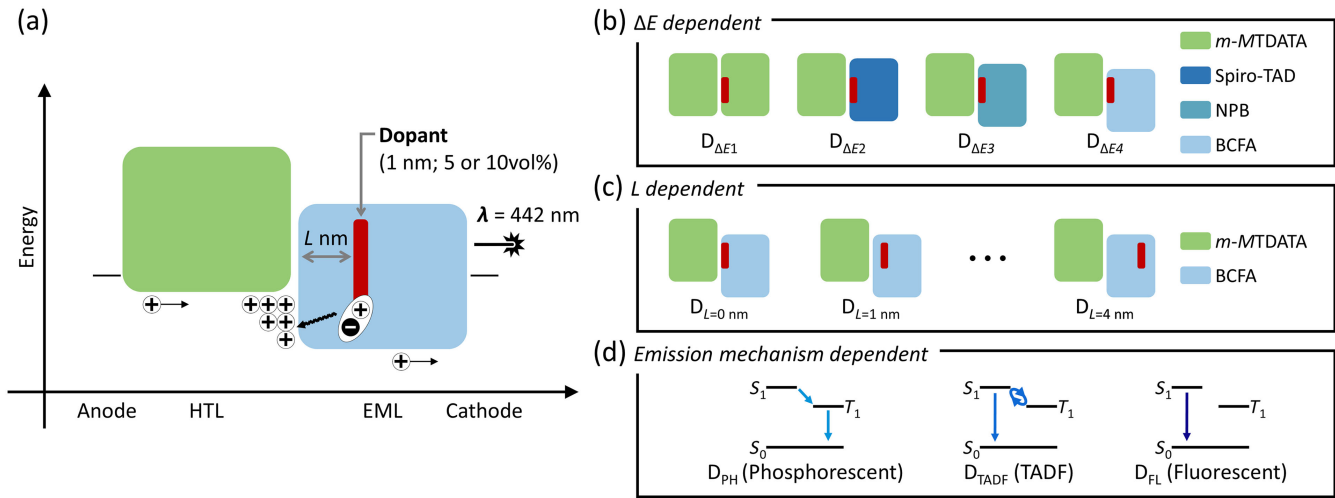


FIG. 1. Bilayer HOD configuration. (a) Schematic representation of a bilayer HOD structure with a 1-nm-thick doped layer inserted within the EML at a distance of L nm from the HTL/EML interface. Positive polaron accumulation at the interface is controlled by the current density applied to the HOD. Excitons are exclusively generated within the doped layer through laser illumination at a wavelength of $\lambda = 442$ nm. (b) Series of HODs featuring different host molecules (m -MTDATA, Spiro-TAD, NPB, and BCFA). (c) HODs with varying dopant positions ($L = 0, 1, 2, \dots, 4$ nm). (d) HODs utilizing different dopants with distinct luminescent mechanisms (phosphorescence, TADF, and fluorescence).

EPQ. Changes in the steady-state PL intensity of the doped layer were recorded by using a fiber-coupled, calibrated spectrometer (FLAME-T-VIS-NIR, Ocean optics) relative to J .

Figure 1(b) shows the structure of four HODs, labeled as $D_{\Delta E1}$, $D_{\Delta E2}$, $D_{\Delta E3}$, and $D_{\Delta E4}$, exhibiting distinct HOMO level offsets (ΔE) at the HTL/EML interface. This result was achieved by varying the host molecules of $D_{\Delta E1}$, $D_{\Delta E2}$, $D_{\Delta E3}$, and $D_{\Delta E4}$ as Tris[phenyl(m -tolyl)amino] triphenylamine (m -MTDATA), 2,2',7,7'-Tetrakis(N,N -diphenylamino)-2,7-diamino-9,9-spirobifluorene (Spiro-TAD), N,N' -Di(1-naphthyl)- N,N' -diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB), and N -([1,1'-biphenyl]-4-yl)-9,9-dimethyl- N -(4-(9-phenyl-9H-carbazol-3-yl)phenyl)-9H-fluoren-2-amine (BCFA), respectively, while keeping the HTL consistent as m -MTDATA. At the HTL/EML interface ($L = 0$ nm) for these HODs, a 1-nm-thick doped layer with a red phosphorescent dopant, Bis[2-(3,5-dimethylphenyl)-4-methyl-quinoline](acetylacetonate)iridium (III) [$\text{Ir}(\text{mphpmq})_2(\text{tmd})$] [36], at a 10 vol% concentration was introduced.

Figure 1(c) shows five HODs incorporating the 1-nm-thick doped layer [$\text{Ir}(\text{mphpmq})_2(\text{tmd})$] at varying distances of $L = 0, 1, 2, 3$, and 4 nm from the HTL/EML interface, denoted as $D_{L=0 \text{ nm}}$, $D_{L=1 \text{ nm}}$, $D_{L=2 \text{ nm}}$, $D_{L=3 \text{ nm}}$, and $D_{L=4 \text{ nm}}$, respectively. Their HTL and host molecules remained consistent as m -MTDATA and BCFA, respectively, exhibiting $\Delta E = 0.31 \pm 0.03$ eV. Utilizing these HODs, the dependence of Inf. EPQ on L —the exciton-polaron separation across the heterointerface—was investigated, providing insights into the critical distance and governing mechanism of Inf. EPQ.

Three HODs were additionally fabricated, each featuring a phosphorescent, fluorescent, or TADF dopant as $\text{Ir}(\text{mphpmq})_2(\text{tmd})$, 10-(benzo[d]thiazol-2-yl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H-pyrano[2,3-f]pyrido[3,2,1-ij]quinolin-11(5H)-one (C545T), and 2,5,15,18-Tetrakis(1,1-dimethylethyl)-10-(2-fluorophenyl)indolo[3,2,1-de]indolo[3',2',1':8,1] [1,4] benzazaborino[2,3,4-kl]phenazaborine (2F-BN) [37], respectively. The luminescent mechanism of each dopant is conceptually depicted in Fig. 1(d). These HODs were labeled as D_{PH} , D_{FL} , and D_{TADF} , with their respective dopant inserted at $L = 0$ nm at a 5 vol%, the level at which excimer formation is restricted, particularly in D_{FL} and D_{TADF} . Commonly, the HTL and host molecules remained consistent as BCFA and tris(4-carbazoyl-9-ylphenyl)amine (TCTA).

Note that material combinations utilized in all HODs were carefully selected to prevent possible exciplex formation among the HTL, host, and dopant molecules. Furthermore, all HTL and host molecules possess higher excited-state energy levels than the dopants, energetically confining excitons within the dopants without back-energy transfer to the other components. Thus, any unintended exciton loss processes were effectively under control in our devices, allowing us to focus solely on Inf. EPQ (see the Supplemental Material [35], Secs. 3 and 4).

III. THEORY

We have developed coupled rate equations to analyze the dynamics of optically generated excitons within the HODs, featuring dopants with diverse luminescent mechanisms. These equations are given as follows:

$$\begin{aligned} \frac{dN_S(x', t, J)}{dt} = & G_{\text{opt}}(x') - k_{\text{ISC}}N_S(x', t, J) + k_{\text{RISC}}N_T(x', t, J) - \frac{1}{\tau_S}N_S(x', t, J) - R(J)N_S(x', t, J) \\ & - \int_0^{d_{\text{HOD}}} k_{\text{EPQ}}(|x - x'|)N_S(x', t, J)p(x, J)dx \end{aligned} \quad (1)$$

$$\begin{aligned} \frac{dN_T(x', t, J)}{dt} = & k_{\text{ISC}}N_S(x', t, J) - k_{\text{RISC}}N_T(x', t, J) - \frac{1}{\tau_T}N_T(x', t, J) - R(J)N_T(x', t, J) \\ & - \int_0^{d_{\text{HOD}}} k_{\text{EPQ}}(|x - x'|)N_S(x', t, J)p(x, J)dx. \end{aligned} \quad (2)$$

Here, N_S and N_T represent the densities of singlet and triplet excitons *within* the doped layer at a specific position x' [or L in Fig. 1(a)]. These exciton densities vary over time (t) on the scale of energy transfer ($\sim \mu\text{s}$) and current density (J) applied to the HODs. The variable p represents the steady-state density of polarons, as a function of J and position x with the range of $[0, d_{\text{HOD}}]$, where d_{HOD} is the total device thickness. Essentially, the presence of excitons does not affect the generation and elimination of polarons (p), rendering p independent of t . Hence, the steady-state polaron distribution (p), at a specific J , is independently determined using a multilayer drift-diffusion model [38–40].

In the model, we assume that the density of states (DOS) for the HTL and EML follow the Gaussian distribution with a common energy disorder σ , and the expected values of these distributions differ by ΔE , representing the average interfacial energy barrier. Polarons are assumed to traverse the HTL/EML interface through either thermally activated uphill or spontaneous downhill hopping, contingent upon the presence of a positive or negative (or zero) energy barrier, respectively, governed by ΔE and σ . The model assuming $\sigma = 0.05$ eV best fits the measured current density-voltage characteristics for our HODs. Compared to the case with $\sigma = 0$ eV exhibiting a step interfacial barrier, a nonzero σ or energetic overlap between the DOS of the HTL and EML better facilitates spontaneous downhill hopping, reducing interfacial polaron accumulation and increasing device conductivity (see the Supplemental Material [35], Secs. 5–8, for the full details of our model).

Singlet excitons (N_S) are initially generated through optical excitation with a rate coefficient G_{opt} . In phosphorescent and TADF systems, singlet excitons can convert to

triplet excitons (N_T) through an exothermic spin-flip process known as intersystem crossing (ISC), which takes place at a rate coefficient k_{ISC} . In the TADF system, a reverse ISC (RISC) is also possible with the assistance of thermal energy at a rate coefficient k_{RISC} . The natural decay times of singlet and triplet excitons are represented as τ_S and τ_T , respectively. The rate coefficient k_{EPQ} quantifies the occurrence of EPQ through Förster resonant energy transfer (FRET) [41] or DET [42]. The FRET- or DET-mediated k_{EPQ} primarily depends on the physical separation ($|x' - x|$) between excitons at x' and polarons at x , which is given by

$$k_{\text{EPQ}}(|x - x'|) = \begin{cases} k_{\text{FRET}} \frac{1}{(x - x')^6} \\ k_{\text{DET}} \exp\left(-\frac{2|x - x'|}{\lambda}\right) \end{cases}. \quad (3)$$

Here, k_{FRET} and k_{DET} are the rate coefficients of FRET and DET, respectively, while λ represents the electronic wavefunction overlap between the excitons at x' and the polarons at x that participate in DET.

In Eqs. (1) and (2), R refers to the rate of field-induced exciton dissociation, an exciton-loss mechanism typically occurring in response to high electric fields beyond 1 MV/cm. Note that R was experimentally determined with respect to J for the cases with phosphorescent, fluorescent, and TADF dopants (see the Supplemental Material [35], Sec. 9, for the detailed methodology).

We have solved Eqs. (1), (2), and (3) for N_S and N_T under steady-state conditions ($t \rightarrow \infty$) with respect to J , which are utilized to account for the normalized PL vs J characteristics of HODs using the following equation:

TABLE I. Given and free parameters used in the model.

Dopant	Given				Free	
	$\tau_S(\text{ns})$	$\tau_T(\mu\text{s})$	$k_{\text{ISC}}(\text{s}^{-1})$	$k_{\text{RISC}}(\text{s}^{-1})$	$k_{\text{DET}}(\text{cm}^3\text{s}^{-1})$	$\lambda(\text{nm})$
Ir(mphmq) ₂ (tmd)	...	1.2 ± 0.1	10^{12} [43]	...	1.0×10^{-12}	1.6
2F-BN	24.1 ± 4.4	126 ± 16	2.0×10^7	2.2×10^4	2.5×10^{-11}	1.7
C545T	2.5 ± 0.4	...	...	...	6.0×10^{-11}	1.6

$$\text{PL}(J)/\text{PL}_0 = \begin{cases} \frac{N_S(J)}{N_S(J=0)} & (\text{TADF, fluorescent OLEDs}) \\ \frac{N_T(J)}{N_T(J=0)} & (\text{Phosphorescent OLEDs}). \end{cases} \quad (4)$$

Here, PL_0 denotes the PL intensity at $J = 0 \text{ mA cm}^{-2}$, where the influence of EPQ is absent. The expression in Eq. (4), henceforth, denotes the $\text{PL}/\text{PL}_0 - J$ characteristics. Note that N_S and N_T correspond to devices featuring fluorescent and phosphorescent dopants, respectively. The given and free parameters for the $\text{PL}/\text{PL}_0 - J$ model are outlined in Table 1.

IV. RESULTS

Figure 2(a) shows the $\text{PL}/\text{PL}_0 - J$ characteristics for $D_{\Delta E1}$, $D_{\Delta E2}$, $D_{\Delta E3}$, and $D_{\Delta E4}$, demonstrating the reduction trend of normalized PL relative to PL_0 , across J values ranging from 10^{-4} to 10^2 mA cm^{-2} . Experimental data are represented by symbols, and solid lines correspond to model fits. The interfacial energy barriers (ΔE) for $D_{\Delta E1}$, $D_{\Delta E2}$,

$D_{\Delta E3}$, and $D_{\Delta E4}$ were determined as 0 , 0.21 ± 0.03 , 0.26 ± 0.03 , and $0.31 \pm 0.03 \text{ eV}$, respectively, through ultraviolet photoelectron spectroscopy measurements (see the Supplemental Material [35], Sec. 5). Notably, as ΔE increased, the PL intensity with increasing J rolled off more dramatically. For instance, at $J = 10 \text{ mA cm}^{-2}$, the PL/PL_0 values for $D_{\Delta E2}$, $D_{\Delta E3}$, and $D_{\Delta E4}$ were reduced by $31\% \pm 2\%$, $53\% \pm 3\%$, and $61\% \pm 2\%$, respectively, relative to those at $J = 0 \text{ mA cm}^{-2}$. The corresponding decrease for $D_{\Delta E1}$ was only $3\% \pm 1\%$. Note that the $J = 10 \text{ mA cm}^{-2}$ corresponds to the injection level required for typical blue PHOLEDs to produce a luminance of $1000\text{--}2000 \text{ cdm}^{-2}$ [44].

In Fig. 2(b), the PL/PL_0 values at $J = 10 \text{ mA cm}^{-2}$ for $D_{\Delta E1}$, $D_{\Delta E2}$, $D_{\Delta E3}$, and $D_{\Delta E4}$ are plotted against ΔE , alongside the model fit calculated using Eq. (4). The PL reduction induced by Inf. EPQ remained minor up to the case with $\Delta E \leq 0.1 \text{ eV}$, including $D_{\Delta E1}$, where polarons can easily surmount the barrier considering the energetic disorder of transport states ($\sigma = 0.05 \text{ eV}$), typical for

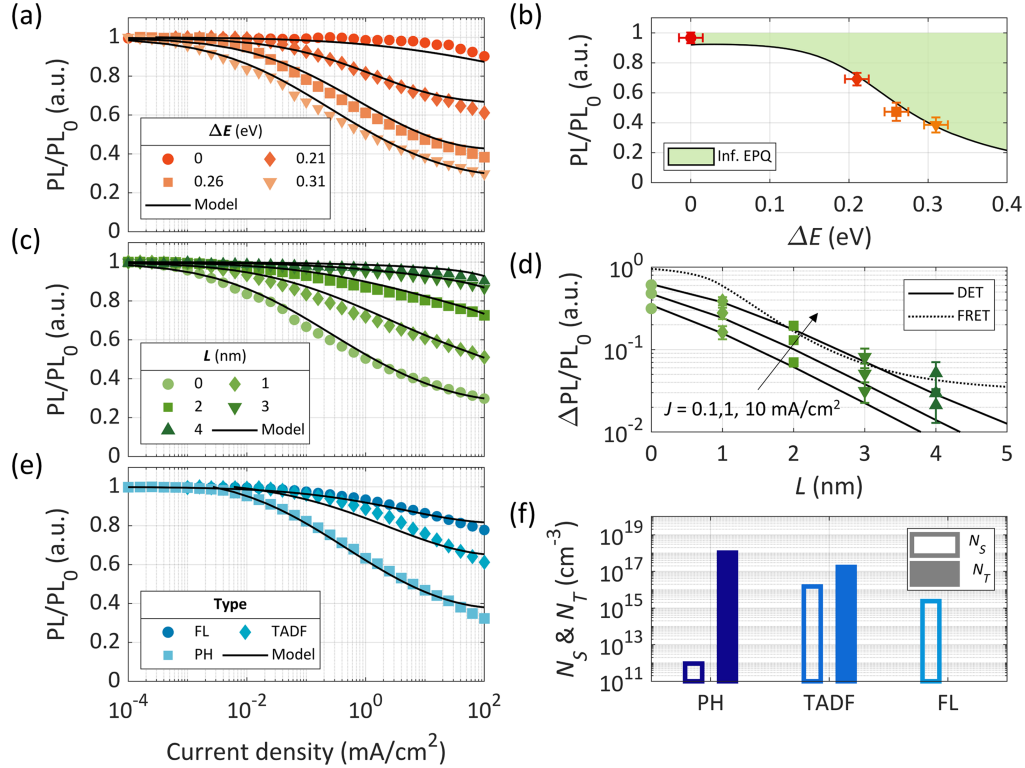


FIG. 2. Photoluminescent characteristics of HODs and modeling analysis. (a) $\text{PL}/\text{PL}_0 - J$ characteristics for $D_{\Delta E1}$, $D_{\Delta E2}$, $D_{\Delta E3}$, and $D_{\Delta E4}$ with $\Delta E = 0, 0.21, 0.26$, and 0.31 eV , respectively (symbols represent the measurement; lines show the model fit). (b) Calculated PL/PL_0 at $J = 10 \text{ mA cm}^{-2}$ as a function of ΔE (symbols show the measurement for $D_{\Delta E1}$, $D_{\Delta E2}$, $D_{\Delta E3}$, and $D_{\Delta E4}$; the green area shows the calculated contribution of Inf. EPQ to the PL reduction). (c) $\text{PL}/\text{PL}_0 - J$ characteristics for $D_{L=0 \text{ nm}}$, $D_{L=1 \text{ nm}}$, $\dots$, $D_{L=4 \text{ nm}}$ with dopant layers positioned at $L = 0, 1, 2, 3$, and 4 nm (symbols show the measurement; the line shows the model fit). (d) Reduction of normalized PL intensity ($\Delta \text{PL} = 1 - \text{PL}/\text{PL}_0$) for $D_{L=0 \text{ nm}}$, $D_{L=1 \text{ nm}}$, $\dots$, $D_{L=4 \text{ nm}}$ at $J = 0.1, 1$, and 10 mA cm^{-2} , plotted against L (symbols show the measurement; solid and dotted lines show DET- and FRET-based models, respectively). (e) $\text{PL}/\text{PL}_0 - J$ characteristics for D_{PH} , D_{TADF} , and D_{FL} (symbols show the measurement; the line is the model fit). (f) Steady-state densities of singlet (N_S) and triplet (N_T) excitons within D_{PH} , D_{TADF} , and D_{FL} calculated at $J = 0 \text{ mA cm}^{-2}$. Error bars in panels (b) and (d) represent 1 standard deviation for at least three devices.

organic semiconductors. However, as ΔE increased beyond 0.2 eV, the effect of Inf. EPQ became pronounced due to increasing interfacial polaron accumulation. For instance, for $D_{\Delta E4}$ with $\Delta E = 0.31 \pm 0.03$ eV, the average polaron density accumulated within a 3-nm range from the interface was estimated at $1.9 \times 10^{18} \text{ cm}^{-3}$, exceeding that for $D_{\Delta E1}$ of $3.5 \times 10^{16} \text{ cm}^{-3}$, by nearly 2 orders of magnitude. Such a discrepancy in polaron accumulation led to a greater exciton loss through Inf. EPQ for $D_{\Delta E4}$ compared to $D_{\Delta E1}$ by a factor of 18.

Figure 2(c) shows the $\text{PL}/\text{PL}_0 - J$ characteristics for $D_{L=0 \text{ nm}}$, $D_{L=1 \text{ nm}}$, ..., $D_{L=4 \text{ nm}}$, with experimental data represented by symbols and solid lines corresponding to model fits. Two distinct trends were observed with respect to L : First, as the doped layer approached the interface ($L \rightarrow 0$), the PL/PL_0 reduction across all J became more pronounced. For instance, at $J = 10 \text{ mA cm}^{-2}$, the PL intensities for $D_{L=4 \text{ nm}}$ vs $D_{L=0 \text{ nm}}$ decreased by $5\% \pm 2\%$ and $61\% \pm 2\%$, respectively, relative to their respective PL_0 . Second, as L increased beyond 4 nm, the $\text{PL}/\text{PL}_0 - J$ characteristics for HODs remained unchanged, commonly having a marginal reduction even at high $J \geq 10 \text{ mA cm}^{-2}$, due to the absence of Inf. EPQ (see the Supplemental Material [35], Sec. 10). This observation suggests a critical distance for Inf. EPQ of around 4 nm.

Figure 2(d) shows the reduction in normalized PL intensity ($\Delta\text{PL} = 1 - \text{PL}/\text{PL}_0$) for $D_{L=0 \text{ nm}} \sim D_{L=4 \text{ nm}}$, plotted against L , measured at $J = 0.1, 1, \text{ and } 10 \text{ mA cm}^{-2}$. Experimental data are represented by symbols, while solid and dotted lines correspond to model fits considering Inf. EPQ through FRET and DET, respectively. Irrespective of injection levels (J), the ΔPL values for these HODs decreased *exponentially* with respect to L . This trend was better explained by the DET-based model with $k_{\text{DET}} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, while the FRET-based model with $k_{\text{FRET}} = 2.1 \times 10^{-13} \text{ cm}^3 \text{ nm}^6 \text{ s}^{-1}$ largely overestimated the data. This result indicates that DET is a primary mechanism of Inf. EPQ in HODs featuring a phosphorescent dopant.

Figure 2(e) compares the $\text{PL}/\text{PL}_0 - J$ characteristics for D_{PH} , D_{TADF} , and D_{FL} , with the largest PL reduction observed in D_{PH} and the smallest in D_{FL} across all J . To explain this difference, we analyzed the densities of singlet (N_S) and triplet (N_T) excitons within D_{PH} , D_{FL} , and D_{TADF} , calculated under steady-state conditions at $J = 0 \text{ mA cm}^{-2}$, as shown in Fig. 2(f). Notably, N_T for D_{PH} was significantly higher at $1.1 \times 10^{18} \text{ cm}^{-3}$, by 2 orders of magnitude, than N_S for $D_{\text{FL}} = 1.5 \times 10^{16} \text{ cm}^{-3}$ and for $D_{\text{TADF}} = 2.4 \times 10^{15} \text{ cm}^{-3}$. This finding is a result of the much longer triplet decay time of $\tau_T = 1.2 \text{ }\mu\text{s}$ for D_{PH} relative to the singlet decay times of $\tau_S = 24.1 \text{ ns}$ and 2.5 ns for D_{TADF} and D_{FL} , respectively [37,45]. Consequently, the most pronounced PL reduction in D_{PH} is because of its long-lived triplets with a substantial density, thereby highly subject to Inf. EPQ. Note that D_{PH} , D_{FL} , and D_{TADF} commonly exhibited a more pronounced PL

reduction as their respective doped layer approached the HTL/EML interface (i.e., $L \rightarrow 0$), confirming that Inf. EPQ is indeed a *universal* phenomenon irrespective of a luminescent mechanism (see the Supplemental Material [35], Sec. 11).

In the comparison between D_{TADF} and D_{FL} , the former exhibited a larger PL reduction across all J compared to the latter [Fig. 2(e)], despite their comparable τ_S and, consequently, similar N_S values. The difference originated from the significant triplet exciton density ($N_T = 1.7 \times 10^{17} \text{ cm}^{-3}$ at $J = 0 \text{ mA cm}^{-2}$) within D_{TADF} stemming via ISC, compared to a negligible ISC rate and consequential $N_T \approx 0 \text{ cm}^{-3}$ within D_{FL} [Fig. 2(f)] [46]. The large N_T within D_{TADF} , even greater than N_S by an order of magnitude, is because the conversion from N_T into N_S via RISC is not as efficient as its competing process through ISC, substantiated by the notably long triplet decay time of $\tau_T = 126 \text{ }\mu\text{s}$ for D_{TADF} . Therefore, a larger PL reduction in D_{TADF} compared to D_{FL} is due to the large density of long-lived triplets, more actively subject to Inf. EPQ without converting into singlets [47–49]. In summary, the extent of PL reduction in D_{PH} , D_{FL} , and D_{TADF} scales with the overall density of singlet and triplet excitons ($S_1 + T_1$), critically determined by the effective decay time of these excitons.

To investigate the impact of Inf. EPQ in practical devices, we fabricated three sets of PHOLEDs: the first with nine red, the second with seven green, and the third with nine blue devices. Each set consisted of PHOLEDs with varying electron blocking layers (EBL) adjacent to the EML, while other layers remained consistent (see the Supplemental Material [35], Sec. 12, for the detailed structures). Through this experiment, we systematically adjusted the interfacial energy barrier ($\Delta E'$) between the EBL and EML HOMOs, allowing for the control of positive polaron accumulation at the EBL/EML interface and consequential Inf. EPQ strength, ultimately determining PHOLED EQE. In order to see this impact more clearly, the PHOLED EMLs were designed to generate excitons near the EBL/EML interface. Nonetheless, we confirmed all EBL materials used effectively prevented the leakage of excitons and negative polarons from the EML (see the Supplemental Material [35], Sec. 13).

Figure 3 shows EQE values plotted against $\Delta E'$ for the red, green, and blue PHOLED sets, measured at $J = 4.8, 1.3$ and 3 mA cm^{-2} , respectively, yielding a luminance of about 1000 cd m^{-2} . Symbols represent experimental data, while the solid line indicates the PHOLED EQE model (see the Supplemental Material [35], Sec. 14). A dashed line parallel to the $\Delta E'$ axis indicates the theoretical EQE limit for the red, green, and blue PHOLEDs at around 23%, 23%, and 20%, respectively. These values took into account an outcoupling efficiency of about 25% and the PL quantum yield of the standalone red, green, and blue EMLs at 91% [50], 90% [51], and 80% [52], respectively, without bimolecular annihilation processes. The reduction in PHOLED EQE relative to its

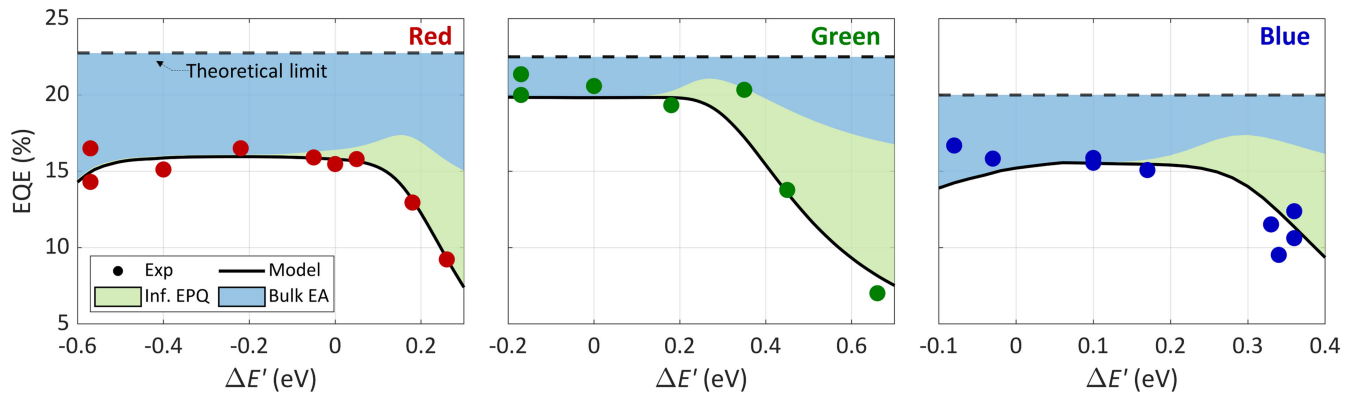


FIG. 3. EQE characteristics of red, green, and blue PHOLEDs. The panels show EQEs of red, green, and blue PHOLEDs with various EBLs at $J = 4.8, 1.3$, and 3 mA cm^{-2} , plotted against the HOMO level offset ($\Delta E'$) between the EBL and EML. The dashed line represents the theoretical PHOLED EQE. (Symbols show measurements; the solid line is the model fit; green and cyan areas show the calculated fractional contribution of interfacial EPQ and other bimolecular reactions occurring within the EML, respectively, to the EQE reduction from the theoretical limit.)

theoretical limit, denoted as ΔEQE , is induced by both Inf. EPQ and bulk exciton annihilation (bulk EA), with their contributions represented as green and blue-shaded areas, respectively (Fig. 3). Note that bulk EA includes all bimolecular annihilation processes occurring *within* the EML, such as EPQ and exciton-exciton annihilation (EEA).

Notably, for $\Delta E' \lesssim 0.10 \text{ eV}$, the EQE values for red, green, and blue PHOLEDs remained nearly consistent at $16\% \pm 1\%$, $20\% \pm 1\%$, and $16\% \pm 1\%$, respectively. Within this range, positive polarons can easily surmount $\Delta E'$ and be injected into the EML without significant accumulation. Therefore, ΔEQE solely arose from bulk EA with the absence of Inf. EPQ. However, as $\Delta E'$ increased beyond 0.1 eV , all devices underwent significant ΔEQE , with a growing impact of Inf. EPQ comparable to or even greater than that of bulk EA. For instance, the ΔEQE values for red, green, and blue PHOLEDs with $\Delta E' = 0.26, 0.45$, and 0.35 eV were $-41\% \pm 3\%$, $-66\% \pm 1\%$, and $-40\% \pm 2\%$, respectively, with the fractional contributions of Inf. EPQ and bulk EA being 52:48, 39:61, and 38:62, respectively.

V. DISCUSSION

To understand the fractional contributions of Inf. EPQ and bulk EA to ΔEQE , we calculated the rates of all possible bimolecular annihilation processes occurring in our blue PHOLEDs possessing $\Delta E' = 0.35$ and 0.25 eV , as shown in Fig. 4. Specifically, bulk EA includes EPQ processes involving positive and negative polarons (denoted as bulk EPQ_+ and bulk EPQ_-) as well as EEA, all occurring *within* the EML. Note that Inf. EPQ can arise due to positive and negative polarons accumulated at the EBL/EML and EML/HBL interfaces, referred to as Inf. EPQ_+ and Inf. EPQ_- , respectively.

For $\Delta E' = 0.35 \text{ eV}$, the effects of bulk EPQ_+ and Inf. EPQ_- were marginal due to an intrinsically low positive

polaron density within the EML and a low exciton density near the EML/HBL interface, respectively. Although the effect of EEA and bulk EPQ_- was considerable, Inf. EPQ_+ proved to be dominant, exceeding the rates of EEA and bulk EPQ_- by 10 and 1.6 times, respectively. On the other hand, with $\Delta E' = 0.25 \text{ eV}$ reduced from 0.35 eV , more positive polarons overcame the interfacial barrier ($\Delta E'$) and were injected into the EML, reducing their interfacial accumulation. Consequently, the effect of Inf. EPQ_+ became relatively diminished, while bulk EPQ_+ emerged

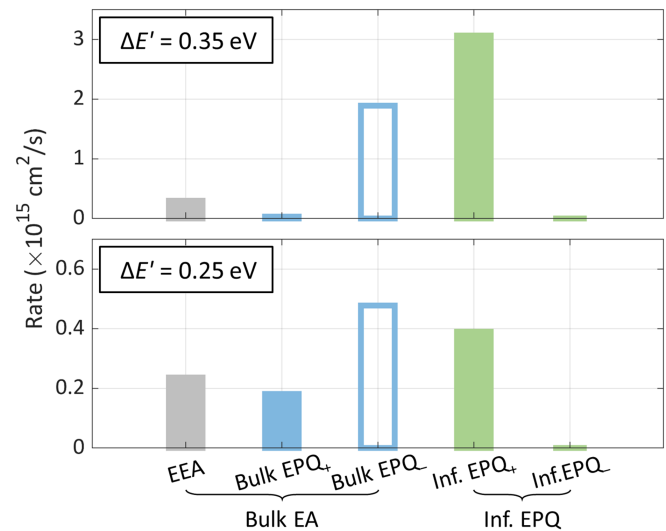


FIG. 4. Bimolecular annihilation processes in blue PHOLEDs. Rates of five bimolecular annihilation processes within blue PHOLEDs possessing $\Delta E' = 0.35$ and 0.25 eV , calculated at $J = 3 \text{ mA cm}^{-2}$, are shown. These processes include EEA, bulk EPQ by positive and negative polarons in the EML (denoted as bulk EPQ_+ and bulk EPQ_-) and interfacial EPQ by positive polarons in the EBL and negative polarons in the HBL (denoted as Inf. EPQ_+ and Inf. EPQ_-).

at a rate of around 40% of bulk EPQ₋. However, the contribution of Inf. EPQ₊ to overall bimolecular annihilation processes remained substantial at around 37%, despite considering bulk EPQ enhancement. This analysis confirms that Inf. EPQ is indeed a crucial factor in determining PHOLED EQE (see the Supplemental Material [35], Sec. 15, for the spatial distributions of polarons and excitons in blue PHOLED).

The efficiency enhancements for OLEDs achieved by mitigating Inf. EPQ lead to the extension of their operational lifetimes. For instance, we achieved around 67% prolonged lifetime for blue PHOLEDs by reducing $\Delta E'$ below 0.1 eV (see the Supplemental Material [35], Sec. 16). This is because the increase in device efficiency corresponds to the decrease in injection levels required to achieve target luminance, thereby minimizing bimolecular annihilations that could otherwise lead to irreversible chemical dissociation.

Note that the densities of positive polarons within the HTL, including those accumulated at the HTL/EML interface, remain consistent as long as the leakage of negative polarons into the HTL is effectively prevented. Thus, the extent of interfacial polaron accumulation, regardless of whether in bilayer HOD or even in full OLED architectures, is primarily governed by the corresponding interfacial energy barrier (see the Supplemental Material [35], Sec. 17).

In addition, even though field-induced exciton quenching was considered in our PL/PL₀ - J model for HODs, its effect was found to be marginal compared to Inf. EPQ. For instance, even at the highest electric field of 9×10^5 V/cm achieved at the injection level of $J = 100$ mA cm⁻² for D_{ΔE4}, field-induced quenching within the phosphorescent dopant takes up less than 5% of total exciton loss, while the major fraction is attributable to Inf. EPQ (see the Supplemental Material [35], Sec. 9).

Mediated by DET with the nonnegligible spectral overlap between the dopant's emission and the HTL cation's absorption, Inf. EPQ may occur through electron exchange between an exciton in the dopant and a positive polaron in the HTL, in such a way to converse their overall spin configurations. Specifically, the high-energy unpaired electron in the dopant exciton transfers to the unpaired HTL HOMO level, forming an electron pair therein. In exchange, one of the paired electrons in the deep-lying HOMO- n level of the HTL is transferred, forming an electron pair with the low-energy dopant electron. As a result, the dopant is deexcited to its ground state, while the HTL is promoted to the energetically hot positive polaron state. To ensure efficient exothermic transition, the overall energy of the system should be stabilized after DET (see the Supplemental Material [35], Secs. 18 and 19, for greater details).

We ensured the reliability of spatial resolution in determining the distance (L) of the doped layer from the interface within HODs to eliminate potential uncertainties associated with vaguely defined organic interfaces. To achieve this goal, we compared the PL/PL₀ - J characteristics of our standard HOD with other cases involving

intermixed HTL, host, and dopant molecules at the HTL/EML interface. Our observations revealed clear differences among these cases, confirming that the standard architecture maintains a well-defined interface without significant intermixing or roughness *beyond* a molecular length scale (see the Supplemental Material [35], Sec. 20).

Additionally, EPQ resulting from spontaneous orientation polarization (SOP) [53,54] can be distinguished as bulk EPQ. Specifically, the polarized CTL via SOP attracts polarons within the EML towards the CTL and induces EPQ within the EML, rather than across the heterointerface as with Inf. EPQ. However, the SOP effect lacks generality and is found only in special cases with preferentially aligned dipoles within organics, such as 1,3,5-tri(phenyl-2-benzimidazoly)benzene (TPBi) [54]. In contrast, whenever a heterointerface exists between the EML and adjacent components, as is typical in standard OLED architecture, we demonstrate that Inf. EPQ universally occurs across various material combinations, even with low-polarity organics like *m*-MTDATA and NPB [53].

V. CONCLUSION

In our study, we have revealed an essential yet often overlooked exciton-loss mechanism in OLEDs termed as Inf. EPQ. This process significantly reduces OLED efficiency by directly transferring the energy of excitons within the EML to polarons within the adjacent CTL. These polarons are likely to accumulate at the interface between these two layers, where an injection energy barrier over 0.2 eV exists. Notably, Inf. EPQ is observed across various luminescent mechanisms, wavelengths, and injection levels. To systematically evaluate its impact under different conditions, we devised a method and device architecture to specifically study Inf. EPQ. Our findings unveil a strong connection between Inf. EPQ and three factors: the interfacial energy barrier, the proximity between excitons and polarons, and the decay time of excitons involved in luminescence. Importantly, we demonstrated that adjusting the interfacial energy barrier has the most significant practical effect, leading to both enhanced efficiency and extended lifetime for PHOLEDs. This study sheds light on the fundamental physics governing exciton-polaron interactions at organic heterointerfaces and presents a feasible solution applicable to a wide range of OLED types, thus advancing the field.

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