

# Excitonic Shockley-Read-Hall Recombination in Organic Semiconductors

Noel C. Giebink<sup>\*1</sup> and Stephen R. Forrest<sup>1,2</sup>

*Department of Electrical Engineering and Computer Science<sup>1</sup>, Physics<sup>1</sup> and Materials Science and Engineering<sup>2</sup>, University of Michigan, Ann Arbor, Michigan 48109, USA*

\*ngiebink@umich.edu

## Abstract

Trap-mediated recombination influences the performance of a wide range of electronic devices. The well-known Shockley-Read-Hall (SRH) expression for inorganic semiconductors is often invoked to describe the recombination rate in organic materials, although without a clear understanding of how its parameters relate to the underlying material properties or how it should be modified to account for the finite lifetime of exciton intermediates in, e.g. the doped emissive layer of an organic light-emitting diode (OLED). Here, we formalize SRH recombination for organic semiconductors based on diffusive trapping and Langevin recombination. We show that including the exciton state suppresses the recombination rate in host-guest systems with type II energy level alignment whenever the interfacial gap between the host and guest molecular orbitals is comparable to the exciton energy. These results quantify the balance between bimolecular and trap-mediated recombination in doped OLED emissive layers, and indicate that devices with type II host-guest pairings can, in principle, beat the thermodynamic limit of their neat guest counterparts.

**Keywords:** trap-mediated recombination, SRH, OLED, host-guest, thermodynamic limit

## I. INTRODUCTION

Trap-mediated recombination is a fundamental process in semiconductor physics that strongly influences the performance of devices such as light-emitting diodes and solar cells [1,2]. The rate of recombination through a discrete trap was established for inorganic semiconductors by Shockley, Read, and Hall (SRH) in 1952 [3,4]. The original SRH expression has since been applied to organic semiconductors in a wide range of contexts, although mostly in qualitative fashion since a rigorous correspondence has yet to be derived for this class of materials [5–11]. One situation of particular interest is the emissive layer of organic light-emitting diodes (OLEDs), where discrete traps are intentionally introduced in the form of emitter dopants in a wide-energy gap host matrix [12]. This situation is related to, but different than the original SRH case because recombination potentially involves two trap levels (i.e. the highest occupied and lowest unoccupied molecular orbital energy levels of the emitter) that are coupled via an exciton state with finite lifetime. Although Monte Carlo and master equation numerical models [13,14] should implicitly account for this difference, a clear physical understanding and analytical expression showing how it affects the trap-mediated recombination rate in organic semiconductors has yet to be established.

Here, we derive the SRH recombination rate explicitly for organic semiconductors and extend it to account for the exciton intermediate state that exists in host-guest emissive systems. We show that including the exciton state reduces the recombination rate in systems that have a type II energy level alignment when the interfacial gap between the host and guest molecular orbitals becomes comparable to the exciton energy. These results rationalize the empirical form of the SRH capture coefficients determined in previous experiments, and quantify the balance between bimolecular and trap-mediated recombination in doped OLEDs. In the radiative limit,

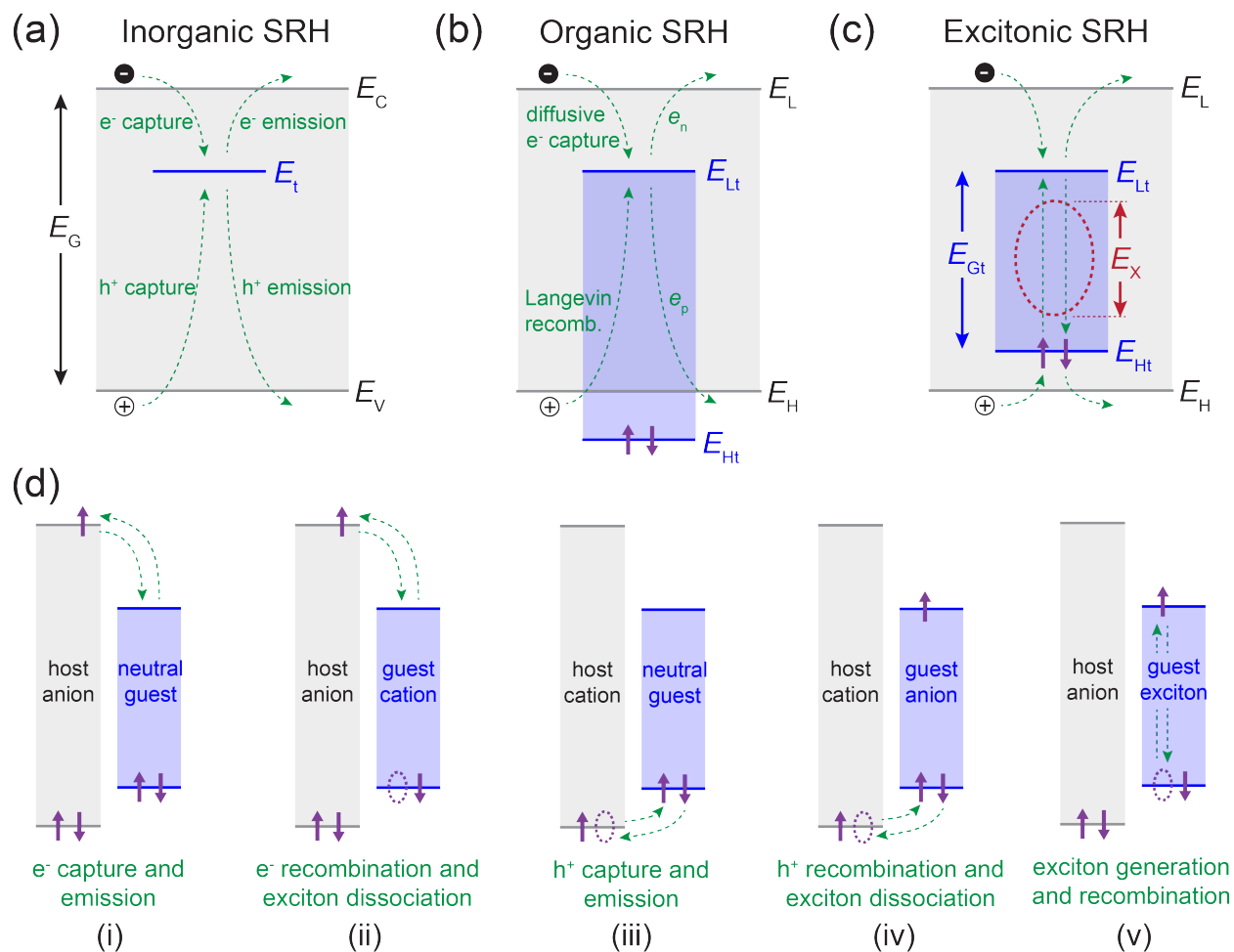
doped OLED emissive layers with nested host-guest energetics (i.e. a type I heterojunction) incur a fundamental overpotential whereas those with staggered, type II energetics can operate at lower voltage than an ideal neat guest device.

## II. RESULTS

The original SRH framework is based on the balance of electron and hole capture and emission rates as illustrated in Fig. 1a for a neutral-when-empty (i.e. acceptor-like) trap level located at energy,  $E_t$ , within the semiconductor bandgap. The analog situation for organic semiconductors is shown in Fig. 1b, where the lowest unoccupied molecular orbital (LUMO) of a closed-shell trap molecule sits within the transport gap ( $E_G$ ) of the host organic semiconductor, and the highest occupied molecular orbital (HOMO) of the trap molecule is sufficiently deep that it does not participate in the recombination process.

The trap-mediated recombination rate in this case follows in analogy to the SRH derivation, except with different capture coefficients. In contrast to the trap cross-section and thermal velocity that characterize electron and hole capture in inorganic semiconductors [1,2], slow hopping transport in organic materials dictates that electrons trap on the guest LUMO in Fig. 1b with the diffusion-controlled rate coefficient,  $C_n = 4\pi D_n R_c$ , where  $D_n = \frac{\mu_n k_B T}{q}$  is the electron diffusion coefficient related to the electron mobility ( $\mu_n$ ) and thermal energy ( $k_B T$ ) by the Einstein relation [12,15]. In the hopping regime, the capture radius of the trap,  $R_c$ , is roughly equal to the dimension of the molecule. Trapped electrons can re-emit at rate  $e_n$ ; however, if a free hole encounters a trapped electron (i.e. an anionic guest molecule), then it will recombine at the reduced Langevin rate,  $\gamma_p = \frac{q\mu_p}{\epsilon}$  set only by the hole mobility since the trapped electron is immobile. Here,  $q$  is the electronic charge and  $\epsilon$  is the dielectric constant. Using the Langevin rate implies that once the trap is occupied (charged), its capture length effectively corresponds to the Coulomb capture

radius. Note that the possibility of double electron trapping (i.e. the formation of a bipolaron) is neglected since it is energetically inaccessible due to the large on-site repulsion of two electrons (i.e. a large Hubbard energy) [15]. Finally, holes may emit from the empty trap LUMO at rate  $e_p$ .



**Figure 1.** (a) Schematic of the capture and emission rates that define SRH recombination through a neutral-when-empty trap level in an inorganic semiconductor. (b) The same rates characterize recombination through an analogous neutral-when-empty LUMO trap level associated with a closed-shell guest molecule (blue) in an organic semiconductor host matrix (gray). Electron trapping in this case is a diffusive process and free hole recombination with a trapped electron proceeds at the Langevin rate. (c) When both the HOMO and LUMO levels of the trap molecule participate, recombination proceeds through an intermediate exciton state. The energy difference

between the HOMO and LUMO levels of the host and guest molecules are their transport gaps,  $E_G$  and  $E_{Gt}$ , respectively. **(d)** Molecular level charge transfer processes involved in excitonic SRH recombination.

Consequently, the steady-state continuity equations for free electrons ( $n$ ) and holes ( $p$ ) are:

$$0 = \frac{1}{q} \nabla \cdot \mathbf{J}_n - C_n n N_t [1 - f(E_{Lt})] + N_t f(E_{Lt}) e_n \quad (1a)$$

$$0 = -\frac{1}{q} \nabla \cdot \mathbf{J}_p - \gamma_p p N_t f(E_{Lt}) + N_t [1 - f(E_{Lt})] e_p \quad (1b)$$

where  $f(E_{Lt})$  is the Fermi occupation function evaluated at the trap energy,  $N_t$  is the density of guest (i.e. trap) molecules, and  $\mathbf{J}_n$  and  $\mathbf{J}_p$  are the local electron and hole current densities, respectively. The last two terms on the right-hand side of Eqn. (1a), respectively, describe the rate of electron trapping in empty guest LUMO levels with bimolecular rate coefficient  $C_n$ , and the rate of electron emission from occupied trap levels. The situation for holes in Eqn. (1b) is similar, except that the hole capture term is given by the Langevin rate associated with an occupied (i.e. negatively-charged) trap. As in the SRH derivation, the emission rates,  $e_n$  and  $e_p$ , are found by evaluating Eqn. (1) at equilibrium where the total current density is zero and the electron and hole capture and emission rates must balance, which yields  $e_n = C_n n_0 \exp\left[\frac{E_{Lt} - E_{Fi}}{k_B T}\right]$  and  $e_p = \gamma_p p_0 \exp\left[\frac{E_{Fi} - E_{Lt}}{k_B T}\right]$  in terms of the equilibrium free electron and hole concentrations ( $n_0$  and  $p_0$ ) and the intrinsic Fermi energy,  $E_{Fi}$ . Subsequently, out of equilibrium when there is net recombination (or generation), the Fermi occupation function of the trap level is found by setting Eqns. (1a) and (1b) equal, which yields  $f(E_{Lt}) = \frac{C_n n + e_p}{C_n n + \gamma_p p + e_n + e_p}$ . The recombination rate is then just the net rate of electron or hole recombination from Eqn. (1a) or (1b):

$$U_{\text{SRH,L}} = \frac{N_t \gamma_p C_n (np - n_0 p_0)}{C_n \left( n + n_0 \exp \left[ \frac{E_{\text{Lt}} - E_{\text{Fi}}}{k_B T} \right] \right) + \gamma_p \left( p + p_0 \exp \left[ \frac{E_{\text{Fi}} - E_{\text{Lt}}}{k_B T} \right] \right)}, \quad (2)$$

where the product of the equilibrium electron and hole densities is the square of the intrinsic carrier concentration,  $n_0 p_0 = n_i^2 = N_h^2 \exp \left( -\frac{E_G}{k_B T} \right)$ , set by the host molecular density ( $N_h$ ) and transport gap,  $E_G$ . Equation (2) is the usual SRH expression, but written in terms of diffusive and Langevin capture coefficients ( $C_n$  and  $\gamma_p$ ) that are meaningful for organic semiconductors. The equilibrium terms in the denominator of Eqn. (2) correspond to the  $n_1$  and  $p_1$  densities used in Refs. [3,5–7,12], with  $n_0$  and  $p_0$  individually determined from charge neutrality as described in Appendix A. In the limit of fast electron trapping ( $C_n \gg \gamma_p$ ) and  $n, p \gg n_0, p_0$ , Eqn. (2) reduces to  $U_{\text{SRH,L}} = \gamma_p N_t p$ , as empirically found in Ref. [5]. When the Einstein relation is valid depending on the degree of energetic disorder [12,16], the ratio of electron and hole capture coefficients in organic SRH recombination thus depends only on temperature and the ratio of their mobilities according to  $\frac{C_n}{\gamma_p} = \left( \frac{4\pi\epsilon k_B T R_c}{q^2} \right) \left( \frac{\mu_n}{\mu_p} \right)$ .

Recombination through a neutral-when-full (i.e. donor-like) HOMO trap located within the host transport gap is analogous in terms of the trap HOMO energy,  $E_{\text{Ht}}$ :

$$U_{\text{SRH,H}} = \frac{N_t \gamma_n C_p (np - n_0 p_0)}{\gamma_n \left( n + n_0 \exp \left[ \frac{E_{\text{Ht}} - E_{\text{Fi}}}{k_B T} \right] \right) + C_p \left( p + p_0 \exp \left[ \frac{E_{\text{Fi}} - E_{\text{Ht}}}{k_B T} \right] \right)}. \quad (3)$$

As usual, recombination is bimolecular in the limit of low electron and hole density, and becomes unimolecular when  $n$  or  $p$  exceeds the right-hand term in either corresponding set of parentheses. Physically, this transition occurs when the electron or hole quasi-Fermi level crosses the trap energy: once full, the recombination rate through that level depends only on the density of the

other carrier. Trap energies located closer to mid-gap are more readily filled at a given quasi-Fermi level splitting and therefore lead to the onset of the unimolecular regime at lower carrier density.

Equations (2) and (3) implicitly assume that a free electron recombining with a trapped hole or vice versa directly produces a guest molecule in its ground state. In the emissive layer of most OLEDs, however, this recombination event results in a guest exciton as shown in Fig. 1c.

The governing rate equations in this case follow from the processes illustrated in Fig. 1d:

$$0 = \frac{1}{q} \nabla \cdot \mathbf{J}_n - C_n n N_t [1 - f(E_{Lt})] + N_t f(E_{Lt}) e_n - \gamma_n n N_t [1 - f(E_{Ht})] + K_{dn} x \quad (4a)$$

$$0 = -\frac{1}{q} \nabla \cdot \mathbf{J}_p - C_p p N_t f(E_{Ht}) - \gamma_p p N_t f(E_{Lt}) + N_t [1 - f(E_{Ht})] e_p + K_{dp} x \quad (4b)$$

$$0 = C_n n N_t [1 - f(E_{Lt})] - N_t f(E_{Lt}) e_n - \gamma_p p N_t f(E_{Lt}) + K_{dp} x \quad (4c)$$

$$0 = C_p p N_t f(E_{Ht}) - N_t [1 - f(E_{Ht})] e_p - \gamma_n n N_t [1 - f(E_{Ht})] + K_{dn} x \quad (4d)$$

$$0 = \gamma_p p N_t f(E_{Lt}) + \gamma_n n N_t [1 - f(E_{Ht})] - (K_{dn} + K_{dp}) x - \frac{x}{\tau} + G_0. \quad (4e)$$

The free carrier Eqns. (4a,b) are analogous to Eqns. (1a,b), except now they include, from left to right, electron trapping and emission from empty guest LUMOs (Fig. 1d,i), recombination of electrons with trapped holes (guest cations) to form guest excitons (Fig. 1d,ii), and dissociation of guest excitons into guest cations and free electrons (Fig. 1d,ii) with rate constant  $K_{dn}$ . Equation (4b) is the same for holes involving capture and emission (Fig. 1d,iii), and recombination and exciton dissociation (Fig. 1d,iv). Equations (4c,d) describe the density of trapped electrons and holes participating in these same processes, and Eqn. (4e) describes the guest exciton density,  $x$ . Guest excitons are generated by electron-hole recombination, they may dissociate into trapped (free) holes and free (trapped) electrons, and they have a thermal generation rate,  $G_0$  (Fig. 1d,v). Together, Eqns. (4a-e) describe detailed balance between free carriers, trapped carriers, and guest excitons. They do not include bimolecular electron-hole recombination on the host and subsequent

energy transfer to the guest since the focus here is on trap-mediated recombination; the relative magnitude of these two recombination pathways is discussed further below.

Adding Eqn. (4a) to Eqn. (4c) in equilibrium shows that  $\gamma_p p_0 N_t f_i(E_{Lt}) + \gamma_n n_0 N_t [1 - f_i(E_{Ht})] + (K_{dn} + K_{dp}) x_0 = 0$ , where  $f_i(E_{Ht})$  and  $f_i(E_{Lt})$  denote the equilibrium trap HOMO and LUMO Fermi-Dirac occupation probabilities, respectively. Thus, by Eqn. (4e), the equilibrium exciton generation rate is just  $G_0 = \frac{x_0}{\tau}$ , where  $\tau$  is the exciton lifetime and the equilibrium guest exciton concentration is given by,  $x_0 = \frac{N_t}{\left[\exp\left(\frac{E_x}{k_B T}\right) + 1\right]}$  in terms of the exciton energy,  $E_x$ , since the exciton chemical potential is zero at equilibrium [17].

The solution procedure going forward is similar to the non-excitonic case: use equilibrium to solve for  $e_n$ ,  $e_p$ ,  $K_{dn}$ , and  $K_{dp}$ , then determine the trap HOMO and LUMO occupation functions and the exciton density out of equilibrium, and finally evaluate the net recombination rate from either Eqn. (4a) or (4b). Beginning with Eqns. (4a-d) in equilibrium, we obtain:

$$e_n f_i(E_{Lt}) + e_p [1 - f_i(E_{Ht})] = p_0 C_p f_i(E_{Ht}) + n_0 C_n [1 - f_i(E_{Lt})] \quad (5a)$$

$$N_t (n_0 \gamma_n [1 - f_i(E_{Ht})] + p_0 \gamma_p f_i(E_{Lt})) = x_0 (K_{dn} + K_{dp}). \quad (5b)$$

Although on the surface Eqns. (5a,b) do not fully determine the equilibrium constants by themselves, detailed balanced implies that the electron emission and trapping terms (left- and right-most) in Eqn. (5a) are equal, as are the hole emission and trapping terms, which yields  $e_n = n_0 C_n \exp\left[\frac{E_{Lt} - E_{Fi}}{k_B T}\right]$  and  $e_p = p_0 C_p \exp\left[\frac{E_{Fi} - E_{Ht}}{k_B T}\right]$ , just as in the isolated trap level case leading to Eqns. (1) and (2) above. The same reasoning between Langevin recombination and exciton dissociation rates in Eqn. (5b) gives  $K_{dn} = \frac{\gamma_n N_t n_0 [1 - f_i(E_{Ht})]}{x_0}$  and  $K_{dp} = \frac{\gamma_p N_t p_0 f_i(E_{Lt})}{x_0}$ . As previously, we recognize that exciton dissociation is not strictly a first order rate process [17], but proceed in the knowledge that this still provides an accurate description at low electric field [18] and is widely

used to describe experimental data [19–21]. Out of equilibrium, Eqns. (4c,d,e) are used to solve for  $f(E_{\text{Ht}})$ ,  $f(E_{\text{Lt}})$ , and  $x$ . Finally, the net recombination rate is obtained by substituting these results back into Eqn. (4a) to get the excitonic SRH recombination rate,  $U_{\text{SRHx}}$ . The expressions for all of these quantities are analytical, but lengthy, and are therefore relegated to the Appendix.

Substantial simplification and insight is possible, however, for the case of a fully symmetric system where the trap levels are nested as shown in the inset of Fig. 2a,i, where  $E_{\text{Fi}}$  lies at mid-gap, the electron and hole mobilities are the same (thus  $\gamma_n = \gamma_p = \gamma$  and  $C_n = C_p = C$ ), and  $n = p$ . The result in this case is:

$$U_{\text{SRHx,sym}} \approx \frac{2N_t\gamma C(n^2 - n_i^2)}{CN_h e^{-\frac{\Delta_H}{k_B T}} + (\gamma + C)n + 2\gamma C\tau N_h \left[ N_h e^{-\frac{E_x - E_{\text{Gt}}}{k_B T}} + n e^{-\frac{E_x - \Delta_{\text{HL}}}{k_B T}} \right]}, \quad (6)$$

where  $\Delta_H$  is the energy difference between the host and guest HOMO (and thus also LUMO by symmetry) levels. In the absence of exciton physics (when  $\tau \rightarrow 0$ ), Eqn. (6) effectively reduces to the sum of Eqns. (2) and (3), which means that, in the limit of infinitely fast exciton recombination, the recombination rate is simply that due to two, isolated HOMO and LUMO trap levels in parallel, referred to hereafter as  $U_{\text{SRH}} = U_{\text{SRH,H}} + U_{\text{SRH,L}}$ . When the exciton has a finite lifetime, the recombination rate is modified through the bracketed term, which depends on the nominal exciton binding energy of the guest,  $E_{\text{bt}} = E_{\text{Gt}} - E_x$ , and an effective binding energy of the blend that involves the host-guest interfacial gap,  $\Delta_{\text{HL}} = E_{\text{L}} - E_{\text{Ht}}$  (Fig. 2a,ii, inset).

For typical exciton energies, host, and guest transport gaps,  $U_{\text{SRHx,sym}}$  is indistinguishable from  $U_{\text{SRH}}$  as shown in Fig. 2a,i. This changes when the guest energy levels are staggered relative to the host as in Fig. 2a,ii and Fig. 2a,iii. In this case,  $U_{\text{SRHx}}$  (now the non-symmetric general case given in Appendix A) is suppressed relative to  $U_{\text{SRH}}$  and the transition from bimolecular to unimolecular recombination in both expressions occurs at progressively lower carrier density as

the guest HOMO level becomes a deeper hole trap. This suppression of  $U_{\text{SRHx}}$  can be understood from the fact that it becomes increasingly favorable for guest excitons to dissociate across the shrinking interfacial gap ( $\Delta_{\text{HL}}$  in Fig. 2a,ii, inset) rather than recombine. This is, in essence, the donor-acceptor (DA) regime of an organic solar cell [12]. Whenever  $\Delta_{\text{HL}}$  is comparable to  $E_x$  and the exciton lifetime is long,  $U_{\text{SRHx}}$  is suppressed relative to  $U_{\text{SRH}}$ , often by orders of magnitude as shown in Fig. 2a,iii and Fig. 2b.

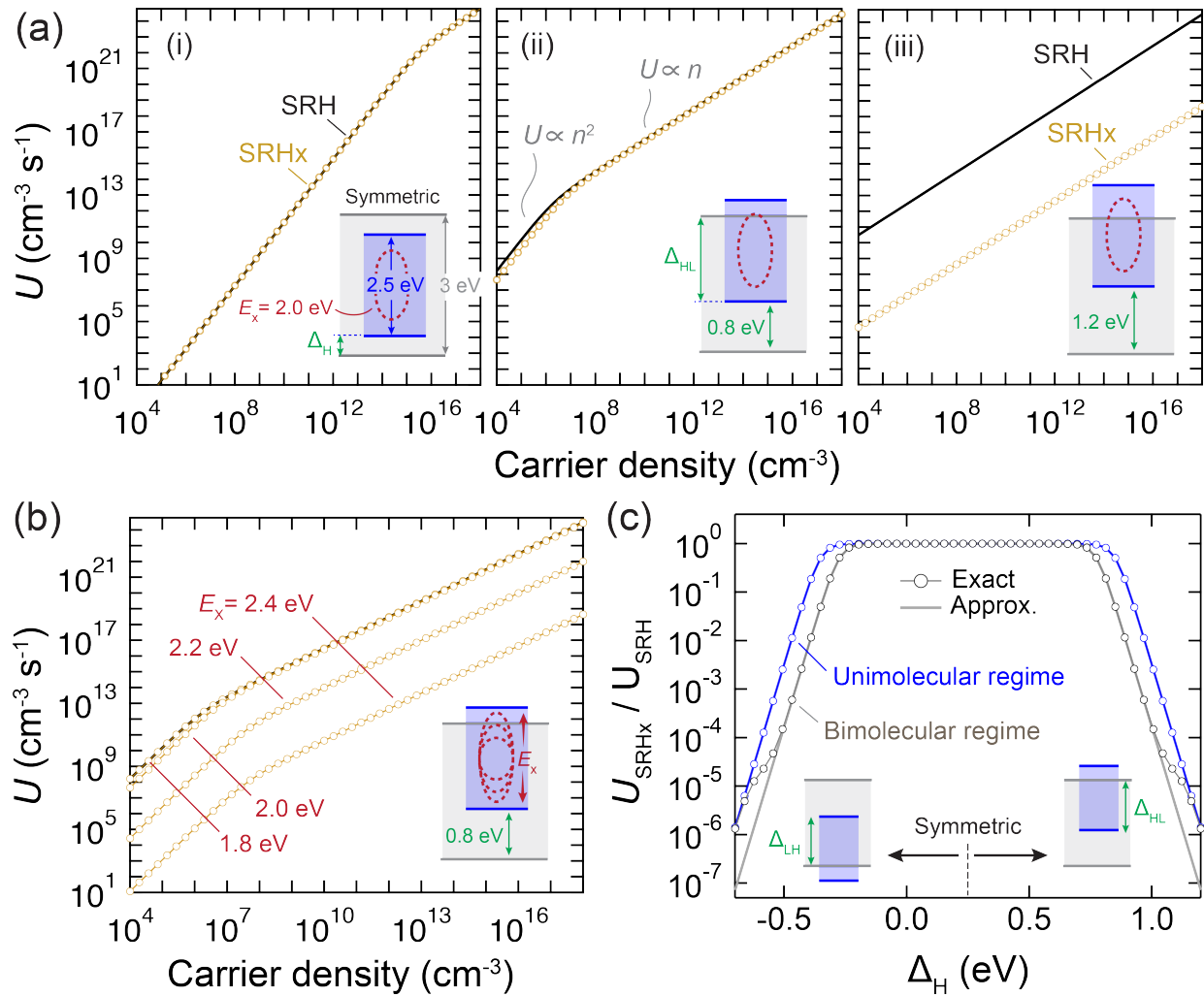
Using Eqn. (6) for guidance, the general case for  $U_{\text{SRHx}}$  can be represented in terms of the base  $U_{\text{SRH}}$  rate modified by an excitonic suppression factor,  $U_{\text{SRHx}} \approx \beta U_{\text{SRH}}$ . The suppression factor is different for the unimolecular and bimolecular regimes, which are respectively given by:

$$\beta_{\text{u}} = \frac{(n\gamma_n + pC_p)(nC_n + p\gamma_p)}{(n\gamma_n + pC_p + p\gamma_n C_p \tau N_h e^{(E_x - \Delta_{\text{HL}})/k_B T})(nC_n + p\gamma_p + n\gamma_p C_n \tau N_h e^{(E_x - \Delta_{\text{LH}})/k_B T})}, \text{ and} \quad (7a)$$

$$\beta_{\text{b}} = \frac{C_p C_n N_h^2}{(C_p N_h + \gamma_n C_p \tau N_h^2 e^{(E_x - \Delta_{\text{HL}})/k_B T})(C_n N_h + \gamma_p C_n \tau N_h^2 e^{(E_x - \Delta_{\text{LH}})/k_B T})}. \quad (7b)$$

In both cases, the dominant scaling comes from the denominator exponential that depends on the effective exciton binding energy of the blend:  $\Delta_{\text{HL}} - E_x$  for systems where the guest energy levels are shifted up relative to the host, and  $\Delta_{\text{LH}} - E_x$  for systems where the guest energy levels are shifted down relative to the host (Fig. 2c, inset). Since only one parenthesis term in the denominator of each expression is significant for a given energetic alignment, it is straightforward to show, e.g. in the common case of a positive offset where  $E_{\text{Lt}} > E_{\text{L}}$ , that  $U_{\text{SRHx}}$  begins to deviate significantly from  $U_{\text{SRH}}$  when the interfacial gap  $\Delta_{\text{HL}} < E_x + k_B T \ln\left(\frac{\gamma_n \tau N_h}{1 + \frac{n\gamma_n}{pC_p}}\right)$  in the low carrier density bimolecular regime, and  $\Delta_{\text{HL}} < E_x + k_B T \ln(\gamma_n \tau N_h)$  in the high carrier density unimolecular regime. As an example, for the parameters used in Fig. 2c, this amounts to  $\Delta_{\text{HL}} <$

$E_x + 0.15$  eV and  $\Delta_{HL} < E_x + 0.23$  eV, respectively. Note that, in the strong donor-acceptor regime (where  $\Delta_{HL}$  is substantially smaller than  $E_x$ ) characteristic of organic solar cells [12,15], the exciton energy and lifetime in these expressions should be associated with the charge transfer state of the blend since that becomes the relevant intermediate for electron-hole recombination. In this case, the trap state is viewed as a two molecule composite: the charge transfer excitation involving both the host and guest corresponds to the guest Frenkel exciton in Eqn. 4, the HOMO of the trap is equal to the guest HOMO (when the guest acts as a donor within an acceptor host), and the LUMO of the trap is equal to the host LUMO.

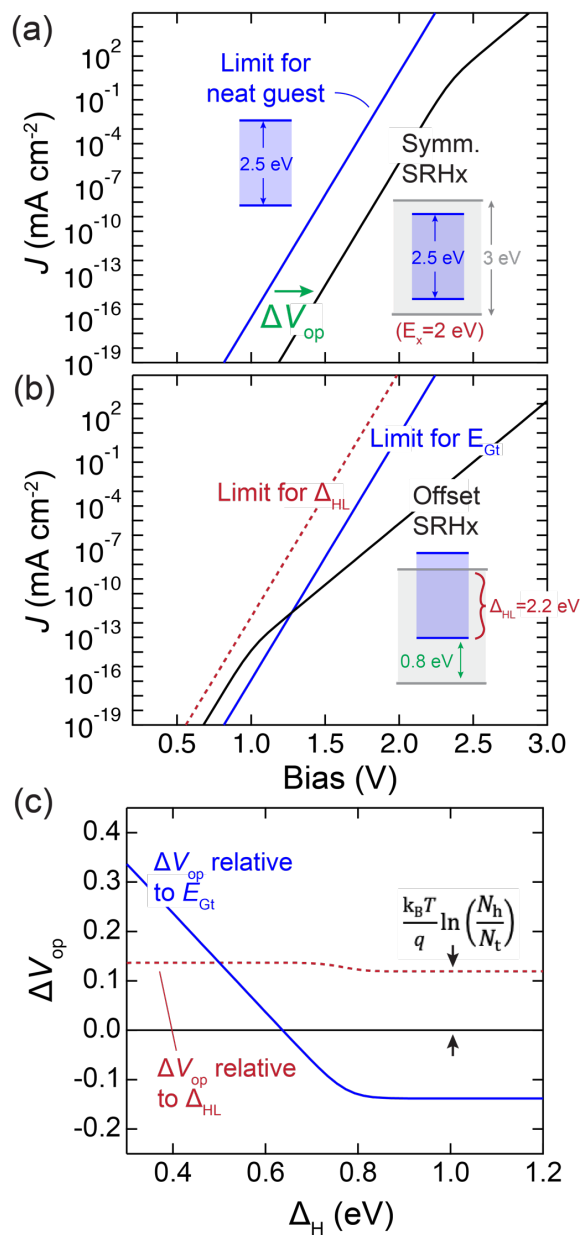


**Figure 2. (a)** Comparison of SRH recombination accounting ( $U_{\text{SRHx}}$ ) and not accounting ( $U_{\text{SRH}}$ ) for involvement of the guest exciton state. When the trap HOMO and LUMO levels are symmetrically nested within the host transport gap (i), there is negligible difference between the two and recombination remains bimolecular up to high carrier density for the shallow trap levels ( $\Delta_{\text{H}} = 0.25$  eV) shown here. As the trap energy levels are increasingly offset from the host in (ii) and (iii), the transition to unimolecular recombination occurs at lower carrier density and  $U_{\text{SRHx}}$  becomes suppressed relative to the non-excitonic case. The exciton, host, and guest transport gaps are fixed at  $E_{\text{x}} = 2$ ,  $E_{\text{G}} = 3$  eV, and  $E_{\text{Gt}} = 2.5$  eV for all cases. **(b)** As the exciton energy grows toward  $E_{\text{Gt}}$  (i.e. the nominal exciton binding energy  $E_{\text{bt}}$  decreases), the recombination rate is increasingly suppressed. When the exciton energy equals the interfacial gap,  $E_{\text{x}} = \Delta_{\text{HL}} = 2.2$  eV, which corresponds to a binding energy of  $E_{\text{bt}} = 0.3$  eV, the suppression factor is roughly 100. **(c)** Comparison of the excitonic suppression factor ( $U_{\text{SRHx}}/U_{\text{SRH}}$ ) in the unimolecular and bimolecular regimes for varying offset energy between the host and guest HOMO levels,  $\Delta_{\text{H}}$ . The symbols show the exact result calculated using Eqn. (A1) from Appendix A and the solid lines show the analytical suppression factor for each regime given by Eqn. (7a,b). All of the plots assume  $\mu_{\text{n}} = \mu_{\text{p}} = 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>,  $\tau = 1$   $\mu$ s, and  $n = p$  for simplicity.

### III. DISCUSSION

Based on these results, it is possible to address the common OLED question of whether light emission in a doped emissive layer originates mainly from exciton formation on the host followed by energy transfer, or from direct charge trapping on the guest [9]. This is readily answered by comparing  $U_{\text{SRHx}}$  with the rate of host bimolecular recombination,  $(\gamma_{\text{n}} + \gamma_{\text{p}})(np - n_{\text{i}}^2)$ . Taking the symmetric case (Eqn. (6)) as an example, but noting that the same qualitative conclusion holds

more generally when  $n \neq p$  as well, the ratio of trap-mediated to host bimolecular recombination is  $\approx \frac{e^{\frac{\Delta_H}{k_B T}} N_t}{N_h}$  in the low carrier density regime (bimolecular SRH) and  $\approx \frac{N_t C}{\gamma n}$  in the high carrier density regime (unimolecular SRH). Thus, for a doping concentration greater than 1% with a HOMO or LUMO trap depth of at least  $\sim 150$  meV, SRH recombination will dominate at room temperature as long as the carrier density remains well below  $N_t$ , which is usually the case for OLEDs in display and lighting applications (i.e.  $n, p < 10^{17}$  cm $^{-3}$  whereas  $N_t = 0.01 N_h \sim 10^{19}$  cm $^{-3}$  in this example). Although  $U_{\text{SRHx}}$  ostensibly falls below the host bimolecular rate in systems with a large suppression factor ( $\beta$ ), it is important to remember that this results from exciton dissociation across the interfacial gap, which will occur in equal measure for guest excitons populated by energy transfer from the host. Thus, excitonic suppression of SRHx does not alter the conclusion that trap-mediated recombination dominates in all but the shallowest trapping cases.



**Figure 3.** (a) Comparison of the current-voltage curve for ideal OLEDs in the radiative limit that employ either a 1 mol% host:guest emissive layer or a neat guest emissive layer. The host:guest system requires an overpotential,  $\Delta V_{op}$ , in order to achieve the same current, and thus light output, as the neat guest device. (b) If the dopant energy levels are offset from the host as shown in the inset ( $\Delta_H = 0.8$  eV, black line), the current in the low voltage bimolecular regime can exceed that of the neat guest device (blue line), leading to a negative overpotential as shown in (c). However,

compared to a neat reference device with a transport gap equal to  $\Delta_{HL}$  (red dashed line) and the same 2.0 eV exciton emission energy, the overpotential is always positive and limits to the entropic penalty associated with the smaller number of dopant recombination sites,  $\left(\frac{k_B T}{q}\right) \ln\left(\frac{N_h}{N_t}\right)$ . All of these plots maintain the same parameters as in Fig. 2, namely  $E_G = 3$  eV,  $E_{Gt} = 2.5$  eV,  $E_x = 2$  eV,  $\mu_n = \mu_p$ ,  $\tau = 1$   $\mu$ s, and  $n = p$ .

These results can also be used to determine whether the thermodynamic limit of an ideal host-guest OLED differs from one made with just the neat guest. Using the fact that  $np = n_0 p_0 e^{\frac{qV}{k_B T}}$  in the absence of any series resistance, Fig. 3a shows the current for a symmetric doped OLED in the radiative limit ( $J = qU_{SRHx}d$ , where  $d$  is the recombination zone width; see Appendix B for details) compared to one employing a neat layer of the same guest molecule, all other factors remaining equal. It is evident that doping introduces an overpotential which, for strong exciton binding, equals  $\Delta V_{op} = \Delta_H + \left(\frac{k_B T}{q}\right) \ln\left(\frac{N_h}{N_t}\right)$  at low current in the bimolecular SRH regime (where the diode ideality factor is unity), and grows linearly with voltage at high current in the unimolecular SRH regime (where the ideality factor is two). Thus, even in the absence of changes in mobility/series resistance/concentration quenching that may result from doping in practice [12], there is a fundamental voltage penalty due the fact that 1) there are fewer recombination sites, and 2) there is an energy loss associated with a host charge carrier that traps on a dopant energy level.

Interestingly, Fig. 3b shows that the same host:guest system with staggered energy levels can exhibit a negative overpotential relative to the neat guest, at least at very low current before the unimolecular overpotential sets in. This occurs because the dopant energy gap (and thus the

neat OLED current) remains the same, but the HOMO trap depth increases, thereby increasing the recombination rate and thus current in the doped device. This reflects the donor-acceptor regime mentioned above in relation to Fig. 2c. From this vantage, the fundamental energy gap for charge carriers in the staggered system is actually  $\Delta_{\text{HL}}$ . If  $\Delta_{\text{HL}}$  is instead taken to be the energy gap of the neat reference device, but the exciton energy is maintained constant so that we are still comparing light output at the same photon energy, then the entropic voltage penalty associated with the smaller number of recombination sites in the doped device (i.e.  $\left(\frac{k_{\text{B}}T}{q}\right) \ln\left(\frac{N_{\text{h}}}{N_{\text{t}}}\right)$ ) re-emerges as shown in Fig. 3c.

At first glance, this ultralow voltage donor-acceptor operating regime would appear to be of limited practical value since it only occurs at very low brightness in Fig. 3b. However, at high enough doping concentration, charge transport can take place via percolation directly on the guest [22,23] (e.g. holes on the guest HOMO in Fig. 2b), which effectively eliminates trapping. Since charge carriers do not trap, recombination is bimolecular (with a Langevin coefficient determined by the effective electron and hole mobilities of the blend [21]) and the voltage penalty associated with unimolecular trap-mediated recombination does not occur. Ultralow voltage donor-acceptor operation (the regime of negative  $\Delta V_{\text{op}}$  for the blue line in Fig. 3c) can therefore persist to high current/brightness in OLEDs with heavily doped or exciplex-type emissive layers as discussed in Ref. [17].

Lastly, although our treatment has focused on the case of a discrete trap to highlight similarities and differences with the traditional SRH model, it could be extended to include energetic disorder with a more realistic distribution of trap energies following the approach in Ref. [12]. In future work, it would be interesting to compare this result to Monte Carlo or master

equation models for varying degrees of trap energy and excitonic disorder to validate the use of disordered excitonic SRH for use in more computationally efficient drift-diffusion models.

#### **IV. CONCLUSION**

In summary, we have formalized SRH recombination for organic semiconductors and extended it to excitonic host-guest systems that are central to the operation of most OLEDs. Inclusion of the exciton intermediate state suppresses the recombination rate in host-guest systems with type II energy level alignment when the interfacial energy gap becomes comparable to the exciton energy. These results quantify the balance between bimolecular and trap-mediated recombination in doped OLED emissive layers and show that offset host-guest systems can, in principle, beat the thermodynamic limit of their neat guest counterparts.

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## **APPENDIX A: FULL EXPRESSION FOR THE EXCITONIC SRH RECOMBINATION RATE**

The general expression for  $U_{\text{SRHx}}$  that results from solving Eqns. (4a-e) is:

$$\begin{aligned}
U_{\text{SRHx}} = N_t \left\{ e^{\frac{2E_{\text{Ht}}+2E_{\text{Lt}}}{k_{\text{BT}}}} \gamma_n C_n C_p (n - n_0) n_0 p + e^{\frac{4E_{\text{Fi}}}{k_{\text{BT}}}} \gamma_p C_n C_p n (p - p_0) p_0 \right. \\
+ e^{\frac{E_{\text{Fi}}+E_{\text{Ht}}+2E_{\text{Lt}}}{k_{\text{BT}}}} \gamma_n C_n C_p n_0 (np - n_0 p_0) + e^{\frac{3E_{\text{Fi}}+E_{\text{Lt}}}{k_{\text{BT}}}} \gamma_p C_n C_p p_0 (np - n_0 p_0) \\
+ e^{\frac{2E_{\text{Fi}}+2E_{\text{Ht}}}{k_{\text{BT}}}} \left( p \left( \gamma_n C_n n \left( (\gamma_p + C_p) n - C_p n_0 \right) + \gamma_p C_p p \left( (\gamma_n + C_n) n - \gamma_n n_0 \right) \right) \right. \\
\left. - \gamma_p C_n n (\gamma_n n + C_p p) p_0 \right) \\
+ e^{\frac{E_{\text{Fi}}+2E_{\text{Ht}}+E_{\text{Lt}}}{k_{\text{BT}}}} \left( p \left( \gamma_n C_n \left( (\gamma_p + C_p) n^2 - C_p n_0^2 \right) + \gamma_p C_p \left( (\gamma_n + C_n) n - \gamma_n n_0 \right) p \right) \right. \\
\left. - \gamma_p C_n n_0 (\gamma_n n + C_p p) p_0 \right) \\
+ e^{\frac{3E_{\text{Fi}}+E_{\text{Ht}}}{k_{\text{BT}}}} \left( np (\gamma_n C_n (\gamma_p + C_p) n + \gamma_p (\gamma_n + C_n) C_p p) \right. \\
\left. - \gamma_n (C_n n (\gamma_p n + C_p n_0) + \gamma_p C_p n_0 p) p_0 - \gamma_p C_n C_p n p_0^2 \right) \\
+ e^{\frac{2E_{\text{Fi}}+E_{\text{Ht}}+E_{\text{Lt}}}{k_{\text{BT}}}} (np - n_0 p_0) \left( \gamma_n C_n C_p (n + n_0) + \gamma_n \gamma_p (C_n n + C_p p) \right. \\
\left. + \gamma_p C_n C_p (p + p_0) \right) \left. \right\} \\
/ \left\{ e^{\frac{2E_{\text{Ht}}+2E_{\text{Lt}}}{k_{\text{BT}}}} C_n n_0 (\gamma_n n + C_p p) + e^{\frac{2E_{\text{Fi}}+2E_{\text{Ht}}}{k_{\text{BT}}}} (C_n n + \gamma_p p) (\gamma_n n + C_p p) \right. \\
+ e^{\frac{E_{\text{Fi}}+2E_{\text{Ht}}+E_{\text{Lt}}}{k_{\text{BT}}}} (C_n (n + n_0) + \gamma_p p) (\gamma_n n + C_p p) + e^{\frac{2E_{\text{Fi}}+2E_{\text{Lt}}}{k_{\text{BT}}}} C_n C_p n_0 p_0 \\
+ e^{\frac{4E_{\text{Fi}}}{k_{\text{BT}}}} C_p (C_n n + \gamma_p p) p_0 + e^{\frac{3E_{\text{Fi}}+E_{\text{Lt}}}{k_{\text{BT}}}} C_p (C_n (n + n_0) + \gamma_p p) p_0 \\
+ e^{\frac{E_{\text{Fi}}+E_{\text{Ht}}+2E_{\text{Lt}}}{k_{\text{BT}}}} C_n n_0 (\gamma_n n + C_p (p + p_0)) \\
+ e^{\frac{3E_{\text{Fi}}+E_{\text{Ht}}}{k_{\text{BT}}}} (C_n n + \gamma_p p) (\gamma_n n + C_p (p + p_0)) \\
\left. + e^{\frac{3E_{\text{Fi}}+E_{\text{Ht}}}{k_{\text{BT}}}} (C_n n + \gamma_p p) (\gamma_n n + C_p (p + p_0)) \right\}
\end{aligned}$$

$$\begin{aligned}
& + e^{\frac{2E_{\text{Fi}}+E_{\text{Ht}}+E_{\text{Lt}}}{k_{\text{B}}T}} \left( C_n(n+n_0) + \gamma_p p \right) \left( \gamma_n n + C_p(p+p_0) \right) \\
& + e^{\frac{2E_{\text{Ht}}+2E_{\text{Lt}}+E_{\text{x}}}{k_{\text{B}}T}} \gamma_n C_n C_p n_0^2 p \tau + e^{\frac{E_{\text{Fi}}+E_{\text{Ht}}+2E_{\text{Lt}}+E_{\text{x}}}{k_{\text{B}}T}} \gamma_n C_n C_p n_0^2 p_0 \tau \\
& + e^{\frac{4E_{\text{Fi}}+E_{\text{x}}}{k_{\text{B}}T}} \gamma_p C_n C_p n p_0^2 \tau + e^{\frac{3E_{\text{Fi}}+E_{\text{Lt}}+E_{\text{x}}}{k_{\text{B}}T}} \gamma_p C_n C_p n_0 p_0^2 \tau \\
& + e^{\frac{E_{\text{Fi}}+2E_{\text{Ht}}+E_{\text{Lt}}+E_{\text{x}}}{k_{\text{B}}T}} n_0 \left( \gamma_n C_p p (C_n(n+n_0) + \gamma_p p) + \gamma_p C_n (\gamma_n n + C_p p) p_0 \right) \tau \\
& + e^{\frac{2E_{\text{Fi}}+2E_{\text{Ht}}+E_{\text{x}}}{k_{\text{B}}T}} \left( \gamma_n C_p n_0 p (C_n n + \gamma_p p) + \gamma_p C_n n (\gamma_n n + C_p p) p_0 \right) \tau \\
& + e^{\frac{2E_{\text{Fi}}+E_{\text{Ht}}+E_{\text{Lt}}+E_{\text{x}}}{k_{\text{B}}T}} n_0 p_0 \left( \gamma_n C_n C_p (n+n_0) + \gamma_n \gamma_p (C_n n + C_p p) \right. \\
& \left. + \gamma_p C_n C_p (p+p_0) \right) \tau \\
& + e^{\frac{3E_{\text{Fi}}+E_{\text{Ht}}+E_{\text{x}}}{k_{\text{B}}T}} p_0 \left( \gamma_n C_n n (\gamma_p n + C_p n_0) + \gamma_n \gamma_p C_p n_0 p + \gamma_p C_n C_p n (p+p_0) \right) \tau \Big\}
\end{aligned} \tag{A1}$$

To evaluate this expression, one needs to know the intrinsic Fermi level position, which in turn determines the equilibrium electron and hole concentrations,  $n_0$  and  $p_0$ . These are found by invoking charge neutrality:

$$n_0 + N_t f_i(E_{\text{Lt}}) = p_0 + N_t [1 - f_i(E_{\text{Ht}})], \tag{A2}$$

which says that the net negative charge due to free and trapped electrons must equal the net positive charge due to free and trapped holes. Using this, together with the fact that  $n_0 p_0 = n_i^2 = N_{\text{h}}^2 \exp\left(-\frac{E_{\text{G}}}{k_{\text{B}}T}\right)$  and  $n_0 = N_{\text{h}} e^{(E_{\text{Fi}}-E_{\text{L}})/k_{\text{B}}T}$  in the Boltzmann approximation, one obtains the position of the intrinsic level in the system:

$$E_{\text{Fi}} = \frac{k_{\text{B}}T}{2} \ln \left[ \frac{N_{\text{h}} e^{-E_{\text{G}}/k_{\text{B}}T} + N_{\text{t}} e^{-(E_{\text{L}}-E_{\text{Ht}})/k_{\text{B}}T}}{N_{\text{h}} e^{-2E_{\text{L}}/k_{\text{B}}T} + N_{\text{t}} e^{-(E_{\text{L}}+E_{\text{Lt}})/k_{\text{B}}T}} \right]. \tag{A3}$$

Using Eqn. (A3), one first finds  $E_{\text{Fi}}$ , then  $n_0$  and  $p_0$ , and finally  $U_{\text{SRHx}}$  from Eqn. (A1).

## APPENDIX B: COMPARISON OF IDEAL DOPED AND NEAT OLEDS IN THE RADIATIVE LIMIT

For an ideal OLED in the radiative limit, every injected charge carrier recombines to emit a photon. Thus, the current for an ideal host-guest OLED where SRH recombination is dominant is simply:

$$J = qdU_{\text{SRHX}}, \quad (\text{B1})$$

where  $q$  is the electronic charge and  $d$  is the width of the recombination zone. The charge carrier densities in Eqn. (A1) are related to the voltage via  $np = n_0p_0e^{qV/k_{\text{B}}T}$  which, if  $n = p$  is assumed for simplicity, provides everything needed to evaluate Eqn. (B1).

The current density due to bimolecular recombination in an ideal neat OLED (with molecular density,  $N_{\text{h}}$ , and transport gap energy,  $E_{\text{G}}$ ) was derived previously in Ref. [17] and is given by:

$$\begin{aligned} J &= qd \frac{(\gamma_n + \gamma_p)}{1 + \tau k_{\text{diss}}} (np - n_0p_0) \\ &= qd \frac{(\gamma_n + \gamma_p)}{1 + \tau k_{\text{diss}}} (N_{\text{h}}^2 e^{-E_{\text{G}}/k_{\text{B}}T}) (e^{qV/k_{\text{B}}T} - 1), \end{aligned} \quad (\text{B2})$$

where  $k_{\text{diss}} = (\gamma_n + \gamma_p)N_{\text{h}} \exp(-E_{\text{b}}/k_{\text{B}}T)$  is the exciton dissociation rate in the bulk that depends on the exciton binding energy,  $E_{\text{b}} = E_{\text{G}} - E_{\text{x}}$ . In both Eqn. (B1) and (B2), the exciton lifetime  $\tau$  is equal to the inverse of the radiative decay rate since the non-radiative decay rate is zero in the radiative limit. Thus, for a given exciton (and therefore emitted photon) energy, it is possible to compare the light output of an ideal doped OLED with its neat dopant analog at a given voltage as done in Fig. 3.

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