Electroluminescence enhancement in polymer light-emitting diodes through hole injection layer insertion

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After a hole injection layer is inserted into a polymer light-emitting diode (PLED), the positive polaron is easily injected into the polymer layer. An applied electrical field drives the positive polaron to approach and collide with the nonemissive triplet exciton. The collision between the positive polaron and neutral triplet exciton induces the exciton to emit light. Based on this physical picture, the maximum quantum efficiency of the PLEDs, 61.6%, is consistent with the experimental result of 60%. With the help of an external magnetic field, a structure of PLEDs with high electroluminescent efficiency is designed. © *2009 American Institute of Physics.*
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I. INTRODUCTION

The sandwich structure of conjugated polymer light-emitting diodes (PLEDs) generally consists of a layer of a luminescent organic conjugated polymer between two metal electrodes.[1] Once electrons and holes are injected into the active polymer layer (APL), electrons attract holes to form pairs, namely, excitons, with radiative decay of the excitons to emit light. The quantum efficiency for electroluminescence can be expressed as $\eta_{EL} = \eta_1 \eta_2 \eta_3$, where η_1 is the ratio of the number of emitted photons over the number of emissive singlet excitons, η_2 is the ratio of the number of optical excitons over the total number of excitons, and η_3 is the ratio of the total number of excitons over the total number of injected carriers.

If exciton recombination in PLEDs is a spin-independent process, there are four possible spin microstates to form excitons, three of which are nonemissive triplet excitons, but only the singlet can decay radiatively, which gives 25% as the maximum of η_2. Thus, the maximum quantum efficiency of the PLEDs is limited to 25%. A recent experiment also confirms this, showing that the singlet fraction in a Alq_3 LED is about 22%.[2] In order to break the limitation of 25%, there are two approaches to take. The first is to synthesize phosphorescent PLEDs that introduces spin-orbit coupling to the polymer. This breaks the original spin conversation and induces the triplet exciton to be an emissive neutral carrier, emitting a photon.[3–5] In phosphorescent PLEDs, the ratio of singlet to triplet excitons is independent of the thickness of the film, temperature, and electric field.[6]

The preference is for the second approach based on the assumption that the singlet exciton is formed with higher probability than the triplet once the binding energy of the triplet exciton becomes weak.[7–9] The prediction indeed was confirmed by an experiment where the electron transport in paraphenylenevinylene (PPV) films is improved and the ratio of electroluminescence with respect to photoluminescence reaches as high as 50%.[10] Through improving the interface at the molecular level in PPV, the ratio of singlet to triplet reached about 45%.[11] Furthermore, it is more surprising that the internal quantum efficiency could be improved to 60% once the hole injection layer (HIL) is inserted in the PLEDs.[12] Based on this progress, the injected charged carriers become the key means for the enhancement in electroluminescence of PLEDs. Moreover, another recent experiment showed that the ratio of singlet to triplet in PLEDs greatly increases once an external electric field is applied, which shows that the enhancement in electroluminescence is a result of the dynamical process driven by the field.[13]

Up to this point, theoretical research and predictions have focused only on the static properties of the electroluminescence of PLEDs (or organic light-emitting diodes in general). Therefore, it becomes necessary to know how carrier motion contributes to the electroluminescence of a PLED, which is also the barrier to understanding the underlying mechanism of breaking the limit of 25% when a hole injection is inserted into a PLED. To clarify this, in this article we develop an approach for molecular dynamics coupled with the electron population rate equations. Based on this, the whole dynamical process can be exhibited after the hole is injected into the PLED, where it is highly possible for the injected polaron to collide with a triplet exciton. It then becomes possible to understand the electroluminescence enhancement in the PLED when the HIL is inserted.

II. FORMALISM

A carrier in a conjugated polymer material is a quasiparticle surrounded by lattice distortion, which is the result of the self-trapping effect. The Su–Schrieffer–Heeger model provides an appropriate and convenient description. However, to include the electron-electron interaction, we have to extend and revise the original model, where we introduce the

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extended Hubbard Hamiltonian (H') as an additional term. The resulting Su–Schrieffer–Heeger–Hubbard Hamiltonian[14] can quantitatively describe the properties of the conjugated polymer. Also, for the confinement effect of a nondegenerate polymer, the Brazovskii–Kirova symmetry-breaking term[15] is added to this model. The resulting Hamiltonian is

$$H = -\sum_{l,s}\{t_0 + \alpha(u_{l+1} - u_l) + (-1)^l t_e\}$$

$$\times [c_{l+1,s}^+ c_{l,s} + \text{H.c.}] + \frac{K}{2}\sum_l (u_{l+1} - u_l)^2 + H' + H_E, \tag{1}$$

$$H' = U\sum_l n_{l,\uparrow} n_{l,\downarrow} + V\sum_{l,s,s'} n_{l,s} n_{l+1,s'}, \tag{2}$$

$$H_E = \sum_{l,s} Ee\left(l - \frac{N+1}{2}\right) a n_{l,s}. \tag{3}$$

Here, t_0 is a hopping constant, α is an electron-lattice coupling constant, $c_{l,s}^+$ ($c_{l,s}$) denotes the electron creation (annihilation) operator at site l with spin s with the corresponding occupation number $n_{l,s} = c_{l,s}^+ c_{l,s}$, a is a lattice constant, u_l is the displacement of atom l with mass M, K is an elastic constant, U and V are the on-site and nearest-neighbor Coulomb repulsion strengths, respectively, E is the electric field strength, N is the number of lattice sites, and t_e is the Brazovskii–Kirova term reflecting the confinement effect in a polymer with a nondegenerate ground state, which ensures that composite particles in the polymer, such as bipolarons or polarons, are stable.[16] Meanwhile, the parameters used in the above Hamiltonian are determined by previous research on conducting polymers. H_E is the interaction of the electrons with the electric field $\vec{E}$ directed along the polymer chain. Since the polymer is not a strongly correlated system, the electron-electron interaction term H' can be treated by the Hartree–Fock approximation[17–19] and thus take the form

$$H' = \sum_{l,s}\left\{U\left(\sum_\mu^{\text{occ}} |Z_{l,\mu}^s|^2 - \frac{1}{2}\right) + V\left[\sum_{s'}\left(\sum_\mu^{\text{occ}} |Z_{l-1,\mu}^{s'}|^2\right.\right.\right.$$

$$\left.\left.\left. + \sum_\mu^{\text{occ}} |Z_{l+1,\mu}^{s'}|^2 - 2\right)\right]\right\} c_{l,s}^\dagger c_{l,s}$$

$$- \sum_{l,s}\left(V\sum_\mu^{\text{occ}} Z_{l,\mu}^s Z_{l+1,\mu}^s\right)(c_{l,s}^\dagger c_{l+1,s} + \text{H.c.}), \tag{4}$$

where Z is an electronic wave function and occ stands for the occupation or electron population.

Generally, molecular dynamics based on the above Hamiltonian can describe in detail the evolution of charge transfer and lattice oscillations. However, we realize that the original molecular dynamics must fix the electron occupation in the relevant energy level, which makes it impossible to depict the process of electron transitions between different levels. In order to resolve this problem, we introduce the electron population rate equations. If there are three energy levels marked by a, b, and c, the evolutions of their related electron populations P_a, P_b, and P_c are presented as

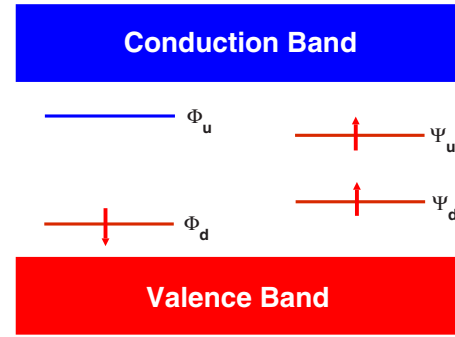$$\frac{dP_a}{dt} = -\gamma_{ab}P_a, \tag{5}$$

FIG. 1. (Color online) Electronic spectrum of the positive polaron and triplet exciton, where the left side refers to the positive polaron and the right side refers to the triplet exciton.

$$\frac{dP_b}{dt} = \gamma_{ab}P_a - \gamma_{bc}P_b, \tag{6}$$

$$P_c = n - P_a - P_b, \tag{7}$$

where γ_{ab} (γ_{bc}) is the transition rate between energy levels a and b (b and c) and n is the total electron number. Using these coupled equations and molecular dynamics, we can quantitatively describe the dynamical evolution of a conjugated polymer chain.

III. RESULTS AND DISCUSSION

In general, the structure of a PLED is composed of three layers, where electroluminescent polymeric materials are inserted between two electrodes. When the conjugated polymer layer is in its ground state, the homogeneous dimerization of the lattice configuration produces about a 1.0 eV gap between the valence and conduction bands. When the bias voltage between two electrodes is applied, electrons and holes are injected into the polymer layer from the negative and positive electrodes, respectively. Then, an electron attracts a hole to form a neutral carrier, leading to two localized states, Ψ_u and Ψ_d, at the center of the band gap. The resultant neutral carrier is called an exciton.

The excitons can be divided into two groups because both the electron and hole are spin carriers with $S = 1/2$, where one is a triplet exciton with $S = 1$ ($S_z = -1, 0, 1$) and the other is a singlet exciton with $S = 0$ ($S_z = 0$). Considering that the formation of an exciton is a spin-independent process, the ratio of the formation of singlet and triplet excitons is 1:3. For the triplet exciton, the spin of an electron in Ψ_u is the same as in Ψ_d, as shown on the right side of Fig. 1. Thus, due to the Pauli exclusion principle, an electronic transition between the two localized states is forbidden so that the triplet exciton is a nonemissive carrier. Because the singlet exciton (25%) is an emissive carrier while the triplet (75%) is not, the maximum quantum efficiency of the PLEDs is limited to 25%. Thus, to induce a triplet exciton to decay radiatively, we try to insert a hole transport layer between the polymer layer and positive electrode of the PLED to introduce a positively charged carrier, such as a polaron, into the polymer.

After a positive polaron is injected into the APL, the whole process can be depicted as followed: one electron at
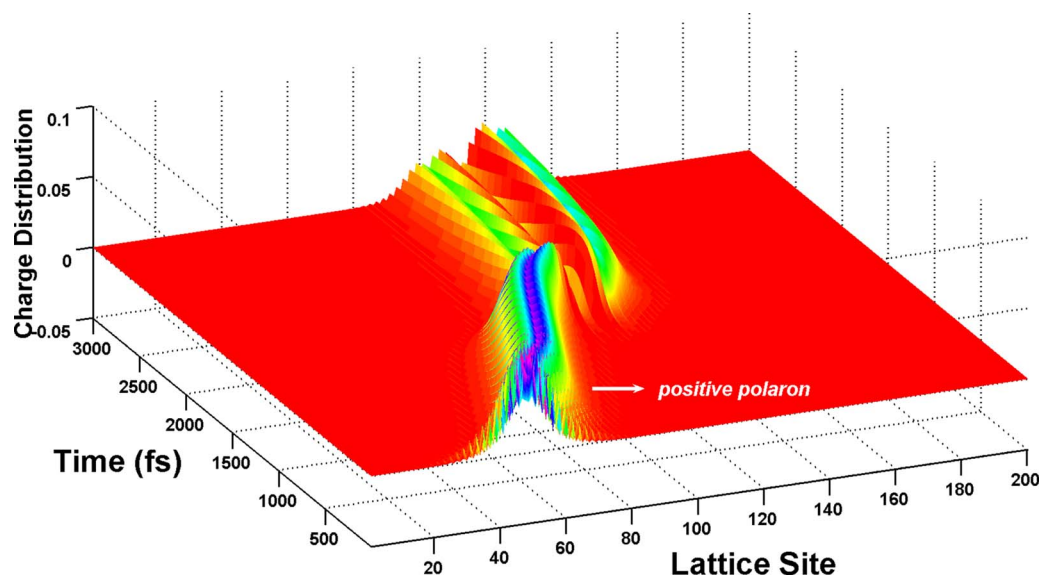
FIG. 2. (Color online) Time-dependent charge distribution of the collision between the positive polaron and triplet exciton under an external field $E=4.0 \times 10^4$ V/cm.

the top of valence band (the highest-occupied molecular or-bital) is removed, and then the self-trapping effect of the conjugated polymer produces two localized states, Φ_u and Φ_d, in the middle of the gap, where Φ_d is occupied by only one electron and the other is empty, as shown on the right side of Fig. 1. The resultant carrier is called a positive po-laron.

It is assumed that there exists at least one triplet exciton in each polymer chain after excitons are formed in the APL. While a positive polaron is injected through the hole trans-port layer, the neutral triplet exciton still resides in the middle of the polymer chain. An external electric field $E=4.0 \times 10^4$ V/cm is applied along the chain, causing the positive polaron to move toward the triplet exciton. As shown in Fig. 1, Φ_d provides an empty place for an electron

with spin up. There is no restriction of the Pauli exclusion principle for this transition, where the electrons in Ψ_u and Ψ_d of the triplet exciton transit to Φ_d once there is a collision between the polaron and exciton.

The whole dynamical process with the time-dependent charge distribution is shown in Fig. 2. Up to 1400 fs, the polaron collides with the neutral triplet exciton. After the collision, the resultant charge $+|e|$ is still localized, but the localization is less than the original polaron, indicating that the result of the collision is a positive-polaron-like carrier. As for the transition of the localized electrons of the triplet ex-citon to Φ_d of the polaron, the rate equations of the devel-oped molecule dynamics provide an efficient tool to depict its entire process, which is described in Fig. 3.

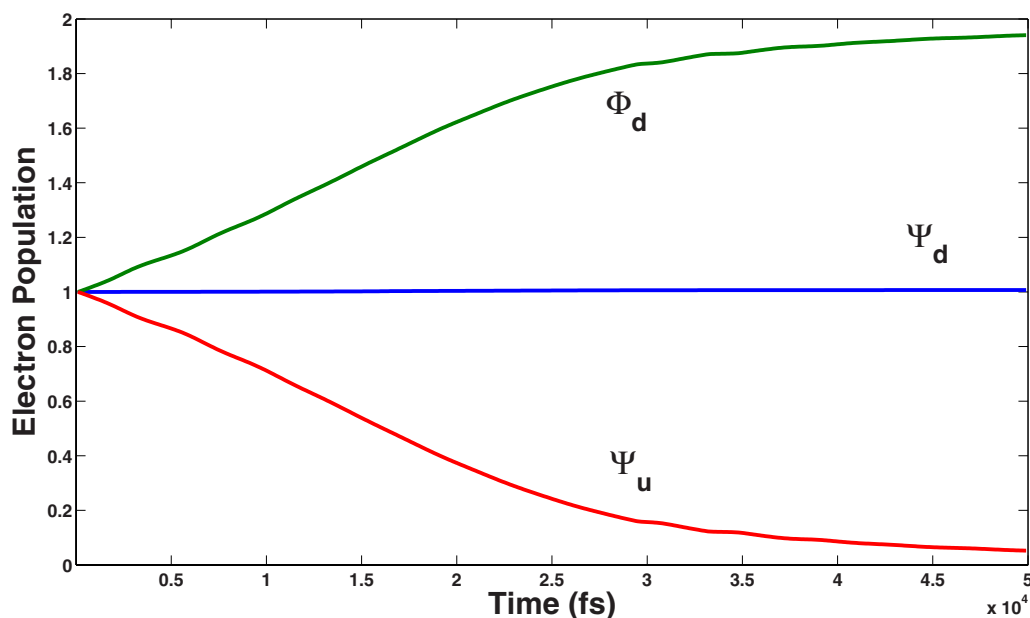Once the positive polaron is injected through the inserted

FIG. 3. (Color online) Time-dependent electron populations in the state Φ_d of the polaron and in Ψ_u and Ψ_d of the triplet exciton once the positive polaron is injected into an APL.
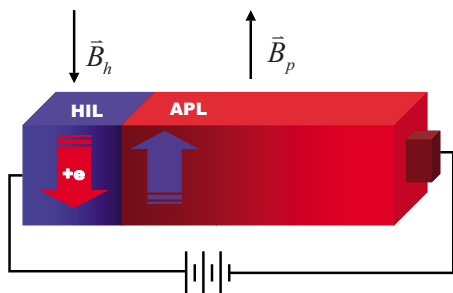
FIG. 4. (Color online) A device of PLEDs used to improve its efficiency of electroluminescence. In the HIL, the spin polarization of the positive polaron is determined by the magnetic field $\vec{B}_h$. The magnetic field $\vec{B}_p$ fixes the spin direction of the triplet exciton in the APL.

hole transport, the electron population in Φ_d of the polaron and in Ψ_u and Ψ_d of the triplet exciton is one. The dynamical process of carrier collision also changes the transition speed, leading to the electronic transition between the localized states at the center of gap, as shown in Fig. 3. During the collision, Ψ_d of the triplet exciton plays a bridgelike role to transfer the electron in Ψ_u to Φ_d of the polaron, emitting photon. After 5×10^4 fs, the population in Ψ_d remains as one, while the electron population in Ψ_u changes to 0.05, and the population in Φ_d becomes 1.94. The collision finally induces the triplet exciton to be an emissive carrier.

The collision-induced emission only happens when the spin of the injected polaron is opposite that of the triplet exciton. If we consider the collision as a spin-independent process, only half of the triplet exciton takes part in the collision and emits a photon. Thus, the obtained quantum efficiency of the PLED is $25\% + 75\% \times [(2-0.05)/2] \times 50\% = 61.6\%$, which is in excellent agreement with the experimental internal quantum efficiency of 60% after the HIL is inserted into the PLED.[11]

With these findings, we propose the following possibility: the efficiency of electroluminescence in PLEDs can be highly improved if the spin of an injected polaron collides with a triplet exciton of opposite spin. In order to tune the spins of the injected polaron and triplet exciton, an external magnetic field can be used to couple with the original sandwich structure of the PLED. The design of an associated device is shown in Fig. 4, where the HIL is inserted between a positive electrode and APL. Most importantly, the magnetic field marked $\vec{B}_h$ is applied to determine the spin polarizations of the injected polaron, and the external magnetic field $\vec{B}_p$ is used to fix the spin polarization of the triplet exciton, as illustrated in Fig. 4. Then, the bias voltage in the junction easily injects the positive polaron from the HIL into the APL where the triplet exciton with opposite spin resides. The collision between the positive polaron and triplet exciton with opposite spin should improve the efficiency of electroluminescence of PLEDs.

In conclusion, after a HIL is inserted into the sandwich structure of a PLED, the positively charged polaron is easily injected into the PLED. Meanwhile, an applied electrical field drives the positive polaron to collide with the neutral triplet exciton, which induces photon emission. The collision improves the internal quantum efficiency to 61.6%, which is consistent with the experiment result of 60%. This collision provides a physical picture to dynamically describe the mechanism of the field-induced electroluminescence enhancement in recent experiments. Finally, a structure of PLEDs with higher electroluminescent efficiency is designed.

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