Singlet and triplet exciton formation rates in conjugated polymer LEDs

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Abstract

Using coupled cluster equation of motion approach, we calculate the formation rates for singlet and triplet excitons associated with intermolecular charge-transfer process. It is found that (i) the interchain bond-charge correlation has a strong influence on the relative ratio, and (ii) on-chain electron-electron correlation and electron-phonon coupling favor singlet exciton formation.

Keywords: Semi-empirical models and model calculations, Many-body and quasiparticle theories.

1. Introduction

It is generally believed that the electroluminescence (EL) efficiency is limited to 25% of that of photoluminescence (PL): for a pair of injected electron and hole, statistically there are 3 triplet states and one singlet state.

Recently, Cao et al. find that the ratio of quantum efficiencies of EL with respect to PL in a substituted polyparaphenylene vinylene (PPV)-based light-emitting-diodes (LEDs) can reach as high as 50%, after blending electron-transport materials into PPV, which is confirmed independently by Ho et al. [1]. They conjecture that either the exciton binding energy is small or that the cross section for an electron-hole pair to form a singlet bound state is significantly higher than that to form a triplet. We note that in conjugated polymers, specifically in PPV, the splittings between the lowest singlet and triplet excitons are around 0.6 – 0.7 eV [2], which is large enough to inhibit any possible contribution from thermalized triplet exciton to luminescence.

We note that in the low energy scattering process of neutron with proton (both with spin ½), the cross section of singlet branch is about 20 times as large as that of triplet [3]. Thus, we propose a scenario that the formation rates for singlet and triplet excitons from free electron hole pair can be different. If it is easier for the singlet pair to bind than

the triplet pair, then the EL over PL efficiency ratio can go beyond the 25% limit [4]. Namely, we propose the limit of this ratio to be $\sigma_S/(\sigma_S+3\sigma_T)$, where σ_S and σ_T are the formation rates for singlet and triplet excitons.

2. Theory and Model

The conjugated system is described by the Pariser-Parr-Pople model:

$$H = -\sum_{<\mu\nu>s} t_{\mu\nu} (c_{\mu s}^+ c_{\nu s} + h.c.) + U \sum_{\mu} n_{\mu\uparrow} n_{\mu\downarrow}$$
$$+ \sum_{\mu<\nu} V_{\mu\nu} n_{\mu} n_{\nu} \tag{1}$$

For PPV, the hopping integrals are set to standard parameters: t_s=-2.2 eV, for single bond, t_d=-2.6 eV for double bond, and t_b=-2.4 eV for phenyl. The e-e interaction is chosen as Ohno-Klopman potential with Hubbard U=11.13 eV.

We take a system consisting two PPV oligomers cofacially separated by a distance of 4 Å, with six phenyl rings each. Suppose initially one chain has a positive charge and another negative (to mimic the charge injection process in LEDs). Through charge transfer processes, this free pair forms an exciton. The initial states are either free triplet or singlet pair. We assume that the total spin is a

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good quantum number, namely, the singlet (triplet) free pair forms only singlet (triplet) exciton as the final state.

We describe the PPV chain, its positive or negative charged states, or the exciton states by the coupled cluster single and double excitation (CCSD) equation of motion (EOM) approach, which is both accurate and size-consistent [5]. The CCSD ground state ansatz is $|CC>=exp(T)|HF>$, where $|HF>$ is the Hartree-Fock Slater determinant, and T is single and double excitations with amplitudes to be solved iteratively. For the excited states and charged states, we construct a CI-like excitation space. We then introduce a general interchain coupling term:

$$H' = -\sum_{\mu\nu} t_{\mu\nu}\, \mu^+\nu + \frac{1}{2}\sum_{\mu\nu\sigma\tau} \langle\mu\nu\,|\sigma\tau\rangle\mu^+\nu^+\tau\sigma \qquad (2)$$

It is understood that each term consists of only mixed chain indices (chain 1 and chain 2). We then apply the Fermi golden-rule to calculate the exciton formation rate: $|<in|H'|fi>|^2$. We do not write down the energy conservation Dirac δ-function explicitly. In fact, both singlet and triplet excitons have finite binding energies. These energies should be dissipated into lattice through electron-phonon coupling in the exciton formation process. Since there exists exchange energy in triplet state, which usually makes the triplet lower in energy than the singlet, it is thus more difficult to form the triplet state, because more phonons are needed, either to be released from the initial state, or to be absorbed by the final state. Thus a first and obvious conclusion can already be drawn that electron-phonon interaction favors singlet formation over triplet. Then, we evaluate the electronic transition matrix. There are two kinds of initial states and final states:

$|in_1>=(|n_2>_\uparrow|p_1>_\downarrow\pm|n_2>_\downarrow|p_1>_\uparrow)/\sqrt{2}$;
$|in_2>=(|p_2>_\uparrow|n_1>_\downarrow\pm|p_2>_\downarrow|n_1>_\uparrow)/\sqrt{2}$;
$|fi_1>=|gs_2>|ex_1>$; $|fi_2>=|ex_2>|gs_1>$.

where $|gs>$, $|n>$, $|p>$, and $|ex>$ represent ground state, negatively charged, positively charged, and excition states, respectively (all of them are obtained through CCSD/EOM). The indices 1, 2 are for chain 1, 2. +/- is for singlet/triplet. It can be seen that $<in_1|H'|fi_1>$ is the rate of exciton formed in chain 1 through electron transport, $<in_1|H'|fi_2>$ is exciton formation in chain 2 through hole transport, etc. We find that for the two-body interchain coupling, the only relevant integral is of the type of [11|12], or [22|21], i. e., the interchain charge-bond interaction, denoted as X in literature [6]. We consider two limiting cases: (i) weak intermolecular coupling, the electronic states are localized on single chains (represented by Eqs. 3a-d); and (ii) strong coupling, the electronic states are coherent combinations of localized states:

$|D_1>=(|fi_1>+|fi_2>)/\sqrt{2}$; $|D_2>=(|fi_1>-|fi_2>)/\sqrt{2}$;
$|D_3>=(|in_1>+|in_2>)/\sqrt{2}$; $|D_4>=(|in_1>-|in_2>)/\sqrt{2}$.
(Note that $<D_1|H'|D_4>=<D_2|H'|D_3>=0$)

3. Results and discussion

The ratios of formation rates between singlet and triplet in different cases are calculated and presented in the Figure. Note that usually X/t is a small quantity. So for electron transport, hole transport, and dark Davydov state ($|D_2>$), the ratio is closed to unity. Only for optically active Davydov state, $|D_1>$, the singlet over triplet formation ratio can be very much enhanced by the charge-bond correlation. Thus the experimental finding of Cao et al. can be explained as following: usually the conjugated polymers are hole transport material and electrons are trapped, Cao et al. blended electron transport materials (to increase the electron-hole pair coherence). It is then $|D_1>$ responsible for the luminescence. In our interchain configuration, the $|D_1>$ is higher than $|D_2>$, thus we expect weak luminescence, again in agreement with Cao et al. [1] margins, page size, and column size etc. as the template already has the correct dimensions.
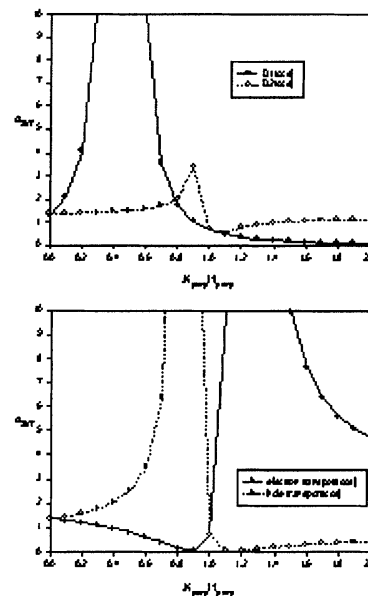

Figure caption: ratio of singlet over triplet exciton formation rates for D_1 and D_2 states (upper panel), and for electron and hole transport (lower panel).

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