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Impurity effects and temperature influence on the exciton dissociation dynamics in conjugated polymers

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ABSTRACT

We investigate temperature effects on exciton dissociation dynamics in conjugated polymer systems. Using a modified version of the tight-binding Su–Schrieffer–Heeger model, the dissociation is studied under the influence of impurity effects with a nonadiabatic evolution method. Our results show that temperature effects reduce the critical electric field for the exciton dissociation. In the small temperature regime, the exciton is not trapped by the impurity and it is observed to perform a random walk, a fact not observed in the absence of temperature. This letter might enlighten the description of electroluminescence yields and charge transport efficiency in organic based electronic devices.

1. Introduction

Conjugated polymers are currently being used as active materials in various optoelectronic devices such as Organic Solar Cells (OSCs) [1], Thin-Film Transistors (TFTs) [2], and Polymer Light-Emitting Diodes (PLEDs) [3]. Singular characteristics, such as light weight, flexibility, versatility of chemical synthesis, and low cost, make them commercially interesting and thus lead to considerable effort in the understanding of how to develop better materials and more efficient devices for the aforementioned class of systems.

In contrast to the conventional inorganic conductors, the fact that conjugated polymer are quasi-one-dimensional materials leads to the novel property of its lattice structure being easily distorted to form self-trapped elementary excitations. This can be accomplished either by charge injections or by a photoexcitation mechanism, and results on the induction of self-localized electron states, such as excitons [4]. In conjugate polymers, an exciton is a bound electron-hole pair state formed due to the strong electron-lattice interactions. It is known that the efficiency of PLDEs and OSCs is related to the exciton dissociation mechanism. A PLED normally consists on a luminescent and a conducting conjugate polymer layer, introduced between two metal electrodes. Electrons and holes are injected from the electrodes into the polymer layer; as a result, this process induce self-localized electron states, which leads to the exciton formation.

In these materials excitons are generally considered to be more strongly localized than excitons in three-dimensional semiconductors, especially because in the former the exciton is substantially confined to a single polymer chain [5]. A schematic energy-level diagram for a PLED under forward bias, that represents the exciton dissociation mechanism in this material, is shown in Fig. 1(a). This phenomenon is accomplished as follows: First, electrons and holes are injected from negative (anode) and positive (cathode) electrodes, respectively (step 1, in the figure). Following, electrons and holes capture one another within the emissive polymer film, and form neutral bound excited state (step 2). Finally, a radiative decay of the excited electron-hole state produced by the recombination process take place (step 3). The spin wavefunction of the exciton, formed from the two spin-$\frac{1}{2}$ electronic charges, can be either singlet ($S = 0$) or triplet ($S = 1$). The radiative emission (fluorescence) is from the singlet only, and when the exchange energy is large, cross-over from triplet to singlet is unlikely to happen, so that triplet excitons do not produce light emission other than by indirect processes such as phosphorescence or by triplet–triplet annihilation [5,6]. In PLEDs The emissive polymer layer generally is formed by a Poly (*p*-phenylenevinylene) (PPV) film, which have high photoluminescence yields [7,8]. The hole transport layer (conducting polymer) widely used in this devices is the Polyaniline (PANI:PPS). Indium-tin Oxide (ITO) is used as the hole-injecting electrode and a magnesium-silver alloy plays the role of the electron-injecting electrode. Considering the OSCs devices, the photovoltaic effect also involves the generation of electron and hole pairs and their subsequent collection at the opposite electrodes [9].

A key aspect in the physics of organic compared to inorganic semiconductors is the difference on the nature of the optically excited states. Whereas in inorganic materials, the production of free charge is carried out directly, the absorption of a photon in organic materials causes a delocalization of these sates, which leads to the formation of an exciton due to the strong electron-lattice interactions. The organic exciton binding energy is naturally large, on the order of or larger than 500 meV. This binding energy represent

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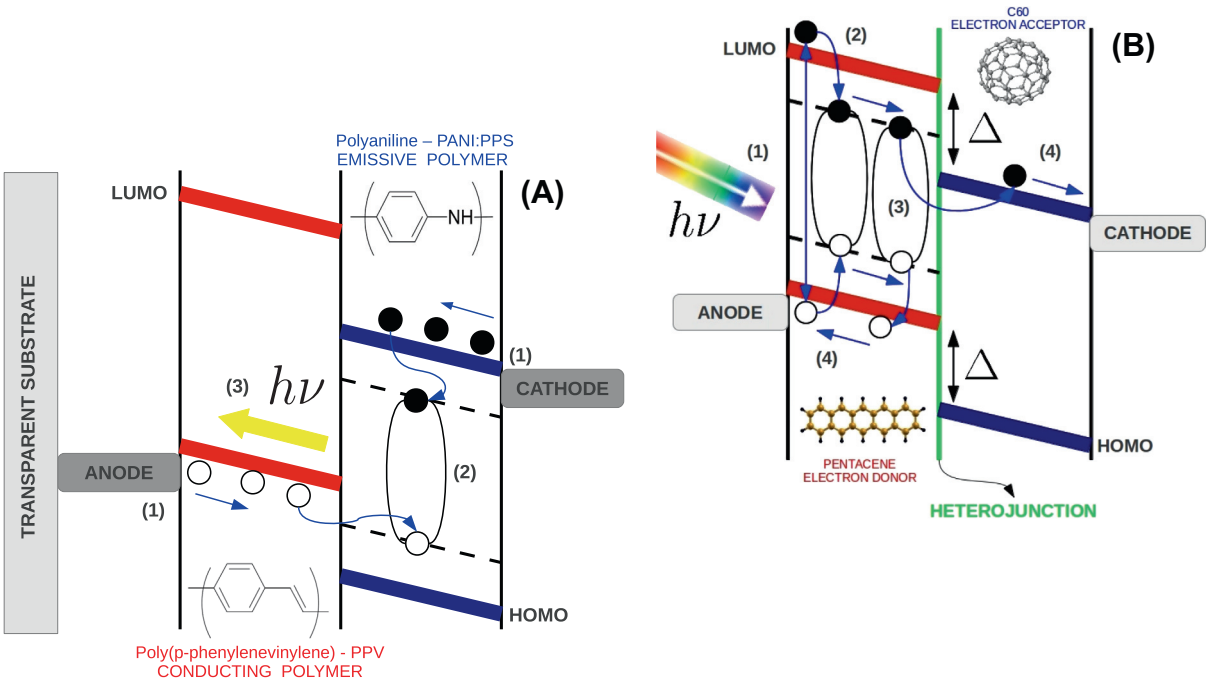

Fig. 1. Schematic energy-level diagram (a) for a PLED and (b) an OSC.

twenty times or more the thermal energy at room temperature, $k_BT(300K) = 26$ meV to be compared with a few meV in the case of inorganic semiconductors [9].

A schematic energy-level diagram for a OSC under illumination, that represents the exciton dissociation mechanism, is shown in Figure 1(b). As a first step (1) the photons are absorbed with an average photon energy larger than the optical band gap on both sides of the heterojunction. Following, occurs the thermalization and the formation of excitons (step 2). The next stage is the excitons diffusion to the heterojunction (3). Finally (4) these structures are dissociated and transfer an electron (hole) into the acceptor (donor) layer. The Δ arrows denote the energy offsets between the ionization potential values (HOMO energies), of the donor molecular layer, and electron affinities (LUMO energies) of the acceptor molecular layer. Figure 1(b) presents a OSC whose conducting polymer layer is formed by a C_{60} film, which have high electron affinity molecules and favors the rapid exciton dissociation, thus resulting in high-power conversion efficiencies [10]. The hole transport layer widely used in these devices is a Pentacene film. The hole-injecting electrode and the electron-injecting electrode are the same in the PLEDs devices.

The above discussions shows that the optical absorption in materials based on conjugated polymers does not lead directly to free electron and hole carriers that could readily generate electrical current. Consequently, to generate current in OSCs, the excitons must first dissociate into free charges. Also, excitons are of great importance in conjugated polymers especially in photoluminescence (PL) emission resultant from the radiative decay of the singlet excitons in PLEDs [11–16]. Furthermore, it has been generally accepted that the temperature effcts are of fundamental importance on monomolecular recombination of mixed states composed by polarons and excitons [17,18]. Thus, the exciton dissociation in the presence of thermal effects are believed to be of fundamental importance for PLEDs. However, studies that take into account this physical picture remains not well described in the literature.

Another question of major importance is the role played by impurity effects on exciton dissociation in conjugate polymers. Zhao et al., using an extended version of SSH model modified to include impurity interactions and the Brazoviski–Kirova symmetry breaking term, investigated the dynamical process of exciton dissociation in the presence of an external electric field [19]. Their results have shown that, under the action of impurities, the stability as well as the effective mass of the exciton is reduced. Also, the field required to dissociate the excitons depends sensitively on the strength of the impurity potential. As the impurity potential strength increases, the dissociation field effectively decreases. In the absence of an impurity in the polymer lattice, the exciton dissociation occurs with an electric field regime of 7.9 mV/Å. Using an impurity strength of 0.25 eV, the critical electrical field decreases to 5.7 mV/Å. Particularly, understanding the effects of the impurity interactions in the presence of thermal effects on exciton dissociation in conjugated polymer systems, is an issue that is believed to be crucial for the design of more efficient devices with respect to the electroluminescence. Thus, this point requires a better phenomenological description.

A relevant theoretical study carried out by Stafström have shown that the exciton dissociation depends crucially on the strength of the applied electric field [20]. An extended version of the SSH model which describes three-dimensional structures was applied to dynamical studies of excited system consisting of two coupled PPV chains. The results showed that the exciton dissociation were not accomplished for field strength lower than 2.0 mV/Åwhereas at 2.8 mV/Åcharge separation was observed to occur within 250 fs. The process of charge separation involves a redistribution of the electrons among the energy levels. This process is field induced but is also strongly dependent on the lattice energy (temperature) and the excitation energy. An increase in these two types of energies both lead to a shortening of the separation time. It is important to remark that all these studies have focused on specific cases with idealized conditions. A theory that widely holds for real materials needs further elements by addressing some realistic effects such as temperature and impurity effects. Also, from these works, we can see that all the results for the exciton dissociation were not fully described, so that further investigation, that take into account temperature effects is needed.