

# Trap effect of triplet excitons on magnetoresistance in organic devices



Fujiang Yang, Gaiyan Zhang, Ruixuan Meng, Kun Gao, Shijie Xie\*

School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

## ARTICLE INFO

### Article history:

Received 24 April 2015

Received in revised form 28 May 2015

Accepted 7 June 2015

Available online 9 June 2015

### Keywords:

Organic bipolar devices

Magnetoresistance

Triplet exciton

Hopping

## ABSTRACT

In an organic bipolar device, injected electrons and holes can form spin singlet and triplet excitons, which are manipulated by an applied magnetic field. We suppose that the localized intra-molecule triplet exciton has a blocking effect on charge carrier transport by assuming that the intra-molecule triplet exciton can increase the on-site binding and make the electron states more localized. By considering the magnetic field-dependent transition between singlet and triplet excitons, from the master equation based on the hopping mechanism, we calculate the magnetoresistance (MR) in organic devices and compare the results with some experimental data. Our research reveals the importance of hyperfine interaction in organic magnetoresistance (OMAR). Especially, our investigation indicates that a bipolar organic device should have a larger MR value than a unipolar one due to the trap effect of triplet excitons on hopping electrons or holes, which is confirmed by some experimental observations.

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## 1. Introduction

Since the discovery of organic magnetoresistance (OMAR) [1,2], there have been persistent experimental [1–8] and theoretical [9–15] investigations on the physical mechanism of OMAR. Up to now, a great number of unipolar [1,16] and bipolar [3,17–20] devices have been fabricated and studied. Several theories have been proposed to explain the effects, involving excitons [3], polaron pairs [21,22] or bipolarons [7]. Usually, magnetoresistance (MR) values around 0–15% are observed in many organic devices, although recent work even predicates an ultrahigh MR value of over 2000% in perfectly one-dimensional molecular devices [23]. In our previous work, we presented theoretical investigations on MR in unipolar organic devices based on hopping theory [24]. For bipolar devices, the main models proposed for OMAR are based on excitons [3,25,26], which suppose that an applied magnetic field causes an additional intersystem crossing between the singlet and triplet states, either at the level of the pair state [25] or at the excitonic level [3]. To explain OMAR, as well as some of the other magnetic field effect, based on the excitons, Desai et al. proposed a triplet-polaron interaction model [3]. While Cox et al. presented a mechanism based on trions, i.e., excited polaron states. They considered reaction between excitons and polarons as spin dependent. By using the drift-diffusion method, MR was obtained [27,28]. In addition, Kalinowski et al. assumed that the singlet exciton dissociation is increased by the magnetic field and then the current is

increased [25]. Hu et al. demonstrated that MR can be changed between positive and negative values by adjusting the dissociation and charge reaction in excited states [17]. In recent years, Keevers et al. studied exciton quenching effect on OMAR. Their work revealed that population mixing due to resonant excitation causes a net change in the exciton-polaron reaction rate [29]. Also, Qin et al. investigated the magnetic field effect through calculation of magnetic field dependent singlet and triplet ratios [30–32]. These indicated the importance of excitons in organic magnetic field effect from either experimental or theoretical aspects. In 2015, Fayolle et al. showed that the interface trap density is important for controlling OMAR and its reproducibility for both unipolar and bipolar devices [33]. A bipolar organic device is different from a unipolar one in that, in a bipolar device, the injected electrons or holes may form various ‘radical pairs’, such as charged electron–electron (or hole–hole) pairs, and neutral electron–hole pairs or excitons. These neutral pairs will block the transport of electrons or holes. Some experimental data seems to indicate that MR value of a bipolar device is larger than that of a unipolar one. For example, Nguyen et al. fabricated Alq<sub>3</sub> devices with different anode and cathode materials to realize a unipolar or a bipolar injection. They found that the MR value is linearly increasing with the exciton/carrier ratio or balance of the device [16]. In this work, we present a quantitatively investigation on OMAR by proposing that, in a bipolar device, there exists an intersystem crossing between singlet and triplet excitons, which is magnetic field dependent. The localized intra-molecule triplet excitons will cause a trap effect on polaron transport. Both singlet and triplet exciton densities are derived from a group of reaction equations based on the

\* Corresponding author.

E-mail address: [xsj@sdu.edu.cn](mailto:xsj@sdu.edu.cn) (S. Xie).

electron–hole interaction, which is dependent upon the applied magnetic field. And then MR is obtained from master equation by calculating polaron mobility, in which the trap effect of triplet excitons on polarons is obtained. In Section 2 we will establish the model and show the calculation methods. The results and discussion are presented in Section 3. Finally a conclusion is made in Section 4.

## 2. Model and methods

Let us consider an organic bipolar device with density  $n_-^0$  and  $n_+^0$  of injected electrons and holes, respectively, in the organic layer at the beginning. Due to electron–hole interaction, they may recombine into a spin singlet exciton or triplet one if an electron encounters a hole. In real process, an electron or hole may firstly form a self-trapped excitation called a polaron, and then a negative and a positive charged polaron form a confined pair prior to the formation of an exciton. In return, an electron–hole pair or an exciton may dissociate into free electrons and holes [17,25]. Singlet and triplet pair densities can be manipulated by the magnetic field. For simplicity, here we leave out the intermediate pair states and only consider the system containing electrons, holes and excitons. Due to the external magnetic field and internal spin related interactions such as spin–orbit coupling and hyperfine field of hydrogen atoms, as well as the spin–spin exchange coupling between two polarons, the statistical yield of the singlet (1/4) and triplet excitons (3/4) will be destroyed [34]. Fig. 1 shows our model describing the formation and dissociation process of singlet and triplet excitons. In linear response approach, we construct the transition equations among the carriers and excitons as,

$$\frac{dn_-}{dt} = -\beta_L n_- n_+ + k_D(E) N_S + k_D(E) N_T \quad (1a)$$

$$\frac{dn_+}{dt} = -\beta_L n_- n_+ + k_D(E) N_S + k_D(E) N_T \quad (1b)$$

$$\frac{dN_S}{dt} = \beta_L \frac{1}{4} n_- n_+ - \gamma_S N_S + \gamma_T N_T - k_D(E) N_S \quad (1c)$$

$$\frac{dN_T}{dt} = \beta_L \frac{3}{4} n_- n_+ - \gamma_T N_T + \gamma_S N_S - k_D(E) N_T, \quad (1d)$$

where  $n_-$ ,  $n_+$ ,  $N_S$  and  $N_T$  are the density of electrons, holes, singlet excitons and triplet excitons, respectively, at time  $t$ . In the right side of Eq. (1a), the first term describes the decrease of electron density due to electron–hole recombination into excitons with recombination coefficient  $\beta_L$ ; the second and third terms represent the

increase due to the exciton dissociation with dissociation coefficient  $k_D(E)$ . The dissociation rate  $k_D(E) = k_0 \left[ 1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \dots \right]$  is related to the electric field, where  $k_0$  is an electric field-independent coefficient,  $b = e^3 E / 8\pi \epsilon_0 \epsilon_r k_B^2 T^2$ , and the summation is the approximation of the first order Bessel function [35,36]. Eq. (1b) has the similar meaning with Eq. (1a). Eq. (1c) describes the change of singlet excitons, where the first term of the right side is due to electron–hole recombination, which is spin-independent, so there is a coefficient 1/4; the second and third term is due to the transition between singlet and triplet excitons, which is spin-dependent; and the last term is due to the dissociation of singlet excitons.  $\gamma_S$  and  $\gamma_T$  are the dissociation rates of singlet and triplet excitons due to their transition.

The transition between singlet and triplet excitons is determined by spin-dependent interactions. Here we consider three interactions: the applied magnetic field, the hyperfine field and the spin exchange interaction, which are described by the following Hamiltonian for a pair of electron and hole,

$$\hat{H} = \sum_{i=1}^2 \left( g\mu_B \hat{S}_{z,i} + a_H \hat{I}_i \cdot \hat{S}_i \right) + J \hat{S}_1 \cdot \hat{S}_2, \quad (2)$$

where  $g$  is the Lande factor,  $\mu_B$  the Bohr magneton,  $a_H$  the strength of hyperfine interaction, and  $J$  the spin exchange interaction of the e–h pair.  $\hat{I}_i$  means spin operator of hydrogen nuclei at site  $i$ . By solving the Schrodinger equation, we obtain the average probability of spin singlet of the pair as  $\bar{p}_S = \frac{1}{16} \left[ 4 - \frac{(\omega^2 + \frac{1}{2}J^2 + \omega J)^2}{4(a_H^2 + \omega^2 + \frac{1}{2}J^2 + \omega J)^2} - \frac{(\omega^2 + \frac{1}{2}J^2 - \omega J)^2}{4(a_H^2 + \omega^2 + \frac{1}{2}J^2 - \omega J)^2} \right]$ , and that of spin triplet state  $\bar{p}_T = 1 - \bar{p}_S$ , where  $\omega = g\mu_B B$  is related to the magnetic field  $B$ . For simplicity we suppose that the dissociation rate is inversely proportional to the pair probability, or,  $\gamma_S/\gamma_T = \bar{p}_T/\bar{p}_S$ .

In the equilibrium state, with the number conservation,  $n_-^0 = n_+ = N_S + N_T$ , we obtain the density of triplet exciton  $N_T$ . In actual materials, the excitons appear in the form of inter-molecule excitons or intra-molecule ones. An inter-molecule exciton is extended over some molecules and is sometimes called electron–hole pair. While an intra-molecule exciton is strongly localized in one molecule, which will form a trap for an electron or hole. For example, an exciton may trap a polaron to form a metastable trion. Therefore, the intra-molecule triplet excitons (a triplet exciton has a much longer lifetime than a singlet one) [3,22] will block the hopping of electrons or holes. If there are more intra-molecule triplet excitons, the blocking effect will be more obvious. To simulate this blocking effect, we consider polaron movement in an organic material with hopping mechanism. Without loss of generality, we assume disordered on-site energies  $\{\epsilon_i\}$  for the molecule in the form of Gaussian distribution of width  $\sigma$  [37]. If there is a triplet exciton at a molecule site, the on-site energy will have a modification of  $-\Delta\epsilon$ . To calculate the mobility in an organic device, we employ the master equation [37–39],

$$\frac{dP_i}{dt} = \sum_{j \neq i} [-\omega_{ij} P_i (1 - P_j) + \omega_{ji} P_j (1 - P_i)], \quad (3)$$

where  $P_i$  is the occupancy number of an electron (hole) at site  $i$ .  $\omega_{ij}$  means the hopping rate from site  $i$  to  $j$ , which is given by the Marcus hopping form,

$$\omega_{ij} = \frac{t_{ij}^2}{\hbar} \left[ \frac{\pi}{k_B T \lambda} \right]^{1/2} \exp \left[ -\frac{(\lambda + \epsilon_j - \epsilon_i)^2}{4k_B T \lambda} \right], \quad (4)$$

where  $\lambda$  is the reorganization energy of the organic material,  $t_{ij} = t_0 \exp(-2\xi_i R_{ij})$  the transfer integral between sites  $i$  and  $j$ ,  $R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$  the distance between the two sites, and  $\xi_i$  is the localization factor of an electron (hole) state centered at site  $i$ . The

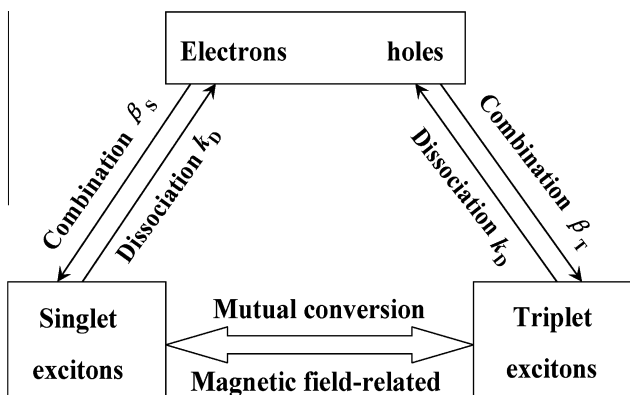


Fig. 1. A schematic diagram of transition among electrons, holes, singlet and triplet excitons in organic semiconductors.

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