Diffusion of excitons in materials for optoelectronic device applications

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Abstract The diffusion of singlet excitons is known to occur through the Förster resonance energy transfer (FRET) mechanism and that of singlet and triplet excitons can occur through the Dexter carrier transfer mechanism. It is shown here that if a material possesses the strong exciton-spin-orbit-photon interaction then triplet excitons can also be transported/diffused through a mechanism like FRET. The theory is applicable to the diffusion of excitons in optoelectronic devices like organic solar cells, organic light emitting devices and inorganic scintillators.

1. Introduction

The performance of many optoelectronic devices depends on the diffusion, radiative recombination and dissociation of excitons. These devices include organic solar cells (OSC) [1], organic light emitting devices (OLEDs) [2], scintillators [3], photo detectors, etc. In these devices excitons are either generated through photoexcitation or charge carrier injection by applying an electric field and after their generation they need to be transported within the device for a certain time or distance. Finally the photo generated excitons dissociate into free electron and hole pairs which are collected at the opposite electrodes of the device, e.g., in OSCs or the electro-generated excitons radiatively recombine by emitting photons, e.g., in OLEDs. In both cases the efficient diffusion of excitons is required for achieving the higher internal quantum efficiency. The exciton transfer can take place via the interaction between an excited molecule or chemical group, say A*, and a ground-state molecule or chemical group, say B, without emitting a photon. Excitons are usually generated in two spin configurations, singlet and triplet. Singlet excitons can recombine radiatively by emitting a photon whereas the radiative recombination of triplet excitons is spin forbidden. This distinction between the singlet and triplet spin configurations affects the way an exciton can move in organic solids from an excited molecule to another molecule in its ground state.

There are two well known models for transfer of excitations in materials. The first model is by Förster [4] and is called the Förster resonance energy transfer (FRET) mechanism where an excited molecule A* gets de-excited and the energy released simultaneously excites another molecule B from
its ground-state due to the Coulomb interaction between the electrons on these two molecules or chemical groups. The second model is due to Dexter [5], where an excited molecule or chemical group exchanges electrons between A* and B to accomplish the non-radiative transfer process. Since the inception of their theories both models have been revisited by many in the literature and the simplest way to achieve the essence of both is by calculating the energy eigenvalue, $W_f(K, S)$ of a Frenkel exciton of spin $S$ (0 for singlet and 1 for triplet) in the real crystal space, where the electron is excited in $f$ state and hole in the ground state $g$ of a molecule in organic solids, which is obtained as [6]:

$$W_f(K, S) = E_g + E_b(S) + L_f(K, S), \quad (1)$$

where $E_g$ is the energy of the band gap, $E_b(S)$ is the binding energy and $L_f(K, S)$ represents the transfer energy of excitons from one molecule to another and is given by:

$$L_f(K, S) = -N^{-1} \sum_{l \neq m} \exp[iK \cdot (l - m)]M_{l,m}^f(S), \quad (2)$$

and

$$M_{l,m}^f(S) = \langle g, l; f, m | U | f, l; g, m \rangle - \langle l, S; g, l; f, m | U | g, m; f, l \rangle. \quad (3)$$

$M_{l,m}^f(S)$ represents the transfer integrals between sites $l$ and $m$ due to the Coulomb potential

$$U = \frac{k e^2}{\eta_2}$$

of interaction between a pair of electrons (e); one in an excited state $f$ and the other in the ground state $g$ and it consists of two terms. The first term represents an e excited in state $f$ on site $l$ and another e in the ground state $g$ on site $m$ initially (right side of $U$) exchange their sites due to the Coulomb interaction, i.e., first e moves to the excited state of $m$ and second moves to the ground state of $l$ (left side of $U$). The second term, which vanishes for the case of triplet spin configuration ($S = 1$), represents where initially the first excited electron in state $f$ on site $l$ (right side of $U$) gets de-excited to the ground state $g$ on site $l$ in the final state (left side of $U$) and the second electron initially in the ground state $g$ at site $m$ (right side of $U$) gets finally excited to state $f$ at site $m$ (left side of $U$). The first term arises due to the exchange interaction between two electrons and it describes the Dexter’s model of transfer of excitons applicable to both singlet and triplet excitons as shown on Fig. 1,
Figure 1. Dexter transfer mechanism due to the exchange interaction (first term of Eq. (3)): (a) for singlet excitons and (b) for triplet excitons

The second term of Eq. (3), which vanishes for triplet excitons, represents the resonance energy transfer as obtained in Förster’s theory. In this case the excited atom at site \( l \) gets de-excited and transfers its energy to excite the molecule at site \( m \) as shown in Fig. 2. Förster’s resonance

Figure 2. Schematic presentation of the Förster resonance energy transfer mechanism for singlet excitons (term 2 of Eq. (3)): excited molecule \( l^* \) gets de-excited and transfers its energy to excite the ground state molecule \( m \) (m* gets excited).

energy transfer is applicable only to singlet excitons because although it is a non-radiative process it requires an excited molecule to get de-excited and the energy is transferred to excite another molecule. This excitation and de-excitation cannot take place if the excited state is a triplet because then such transitions would be spin forbidden, as it can also be seen from Eq. (3) that for \( S = 1 \) the second term vanishes. It may be noted that it is the term \( L_f(K, S) \) in Eq. (2) that contributes to the kinetic energy of an exciton with an effective mass in a lattice [6]. For non-crystalline solids the wave vector \( K \) is not relevant but the matrix element \( M_{l,m}^f(S) \) still has the same significance as described above [6-7].
However, recently the Förster resonance energy transfer (FRET) has been applied to interpret the photoluminescence kinetics in OLEDs [8] and inorganic scintillators [9], e.g., CdWO$_4$ and in both cases triplet Frenkel excitons are excited. In OLEDs the host or donor material is doped with compounds containing heavy metal atoms. The purpose of this paper is to illustrate that under the influence of strong exciton-spin-orbit-photon interaction, excitons either excited by photons (electro-magnetic field) or by injecting the charge carriers (electric field) as in OLEDs, FRET can be used to study the transfer of triplet excitons as well.

2. Effect of Spin-orbit interaction

The derivation of the time-dependent exciton-spin-orbit interaction is briefly described here and the details are published in [10]. For a pair of excited electron and hole in a solid with $N$ atoms/molecules, the stationary spin-orbit interaction denoted by $H_{so}^{sol}$ can be written as [10-11]:

$$\hat{H}_{so}^{sol} = -\frac{eg}{2\mu_{x}c^{2}}s_{e} \cdot (p_{e} + e/c A_{e}) \times (\sum_{n=1}^{N} \frac{1}{c} \frac{\partial A_{e}}{\partial t} - \sum_{n=1}^{N} \nabla V_{ne}) + \frac{eg}{2\mu_{x}c^{2}}s_{h} \cdot (p_{h} - e/c A_{h}) \times (\sum_{n=1}^{N} \frac{1}{c} \frac{\partial A_{h}}{\partial t} - \sum_{n=1}^{N} \nabla V_{nh}) ,$$

(4)

where $\mu_{x}$ is the reduced mass of an exciton (electron and hole), $g$ is the gyromagnetic ratio ($g = 2$), $s_{e}$ and $p_{e}$ are the spin angular and orbital momenta of the electron, respectively, and $s_{h}$ and $p_{h}$ are those of the hole and $E_{ne}$ and $E_{nh}$ are the electric fields experienced by the electron and hole, respectively, due to the nucleus. When an electromagnetic radiation incidents on the sample, Eq. (4) modifies to:

$$\hat{H}_{so}^{sol} = -\frac{eg}{2\mu_{x}c^{2}}s_{e} \cdot (p_{e} + e/c A_{e}) \times (\sum_{n=1}^{N} \frac{1}{c} \frac{\partial A_{e}}{\partial t} - \sum_{n=1}^{N} \nabla V_{ne}) + \frac{eg}{2\mu_{x}c^{2}}s_{h} \cdot (p_{h} - e/c A_{h}) \times (\sum_{n=1}^{N} \frac{1}{c} \frac{\partial A_{h}}{\partial t} - \sum_{n=1}^{N} \nabla V_{nh}) .$$

(5)

In obtaining Eq. (5), it is found that the influence of the magnetic field in the radiation vanishes [10-11]. Therefore, it is anticipated that the results are also applicable for the case of generation of electrons and holes by an electric field alone. The time-dependent exciton-photon-spin-orbit interaction extracted from Eq. (5) is thus obtained [10]:

$$\hat{H}_{so}^{sol(t)} = -\frac{e^{3}gk}{2\mu_{x}c^{2}} \sum_{\lambda,n} \left( \frac{2\pi}{\epsilon_{0} \epsilon_{0}^{2}\epsilon^{2} V} \right)^{1/2} \sin \phi_{\lambda e n} s_{ee} \left[ e^{-i \omega_{\lambda} \lambda t} c_{\lambda}^{+} \right] + \sum_{\lambda,n} \left( \frac{2\pi}{\epsilon_{0} \epsilon_{0}^{2}\epsilon^{2} V} \right)^{1/2} \sin \phi_{\lambda h n} s_{h h z} \left[ e^{-i \omega_{\lambda} \lambda t} c_{\lambda}^{+} \right] .$$

(6)

Using the triplet spin configuration and the property of $s_{ee}$ and $s_{h h z}$ spin operators as $s_{ee}d_{e}(\pm \frac{1}{2}) = \pm \frac{1}{2} \hbar a_{e}(\pm \frac{1}{2})$ and $s_{h h z}d_{g}(\pm \frac{1}{2}) = \pm \frac{1}{2} \hbar d_{g}(\pm \frac{1}{2})$, we find that the triplet spin
configuration of a triplet exciton gets flipped to the singlet spin configuration due to the spin-orbit interaction and the time-dependent operator in Eq. (6) becomes [10-11]:

$$
\hat{H}_{SO}^{sol(t)} \approx -\frac{2\hbar^2 gZ\kappa}{\mu^2} \left( \frac{2\pi\hbar}{e_0 e V} \right)^{1/2} \sum \frac{\sin \lambda}{\sqrt{\omega_\lambda}} e^{-i\omega_\lambda t} \times \left[ \frac{1}{\sqrt{2}} (a_e (+1/2)d_g (-1/2) + a_e (-1/2)d_g (+1/2)) \right] c_\lambda^+.
$$

(7)

Thus the mechanism of the radiative recombination of triplet excitons through the time-dependent transition operator can be described in the following two steps:

1. The new operator is attractive for excitons so it attracts a triplet exciton to the heaviest atom as it is proportional to the atomic number. As the magnitude of attraction inversely proportional to the square of the average distance between an electron and nucleus, only the nearest heavy nucleus will play the dominant role.

2. As soon as a triplet exciton interacts with such a spin-orbit-exciton-photon interaction, the spin gets flipped to a singlet configuration and exciton recombines radiatively by emitting a photon.

As the spin of the triplet exciton is flipped the electron and hole can recombine either radiatively to emit photons or get transferred non-radiatively by following Förster’s resonance energy transfer mechanism. In this way the strong exciton-spin-orbit-photon interaction enables FRET mechanism to be applicable to triplet excitons as well.

3. Results and discussions

It is shown here that the effect of the time-dependent spin-orbit interaction on triplet excitons is that it flips the spin to singlet configuration and then they behave like singlet excitons as shown in Fig. 3.

**Figure 3.** Effect of the time-dependent exciton-spin-orbit-photon interaction on triplet excitons: It flips the spin to singlet configuration.

In organic solids used for the fabrication of organic solar cells (OSCs) it has been observed that the conversion efficiency of OSCs gets enhanced if the donor is incorporated with heavy metal atoms [11-15]. As the time-dependent spin-orbit interaction in Eq. (4) is proportional to the atomic number $Z$, doping with heavy metal atoms enhances the effect of spin-orbit interaction and hence triplets are converted into singlets which diffuse faster through FRET than triplet excitons [11]. This results in a faster diffusion of excitons to the donor-acceptor interface resulting in faster dissociation and hence higher conversion efficiency. The triplet excitons transfer occurs through the Dexter mechanism which depends on the exchange interaction which is known to be a short range interaction [6, 8] and hence it is effective only at short distances, i.e., between nearest neighbors with overlapping electronic wave functions [8].
In OLEDs it is very well established that the emission efficiency gets enhanced when doped with heavy metal atoms like platinum (Pt), iridium (Ir) and palladium (Pd) [16,19], which has been attributed to the conversion of triplet excitons to singlets whose radiative recombinations are spin allowed [2, 20] as presented above. In inorganic scintillators, the transfer of triplet excitons in CdWO₄ can be better explained in terms of Förster’s mechanism [9], which is based on the dipole-dipole interaction as is well known [8]. Inorganic solids have usually higher atomic numbers and hence stronger spin-orbit interaction which again converts triplets into singlets and then get transferred efficiently through the Förster mechanism.

4. Conclusions
It is shown that the time-dependent exciton-spin-orbit interaction, which depends on the atomic number, assists flipping the spin of triplet excitons to singlet spin configuration and hence the Förster mechanism can be applied for the transfer of triplet excitons as well. Present results can successfully explain many experimental results in OSCs, OLEDs and inorganic scintillators.

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