Roles of binding energy and diffusion length of singlet and triplet excitons in organic heterojunction solar cells

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1 Introduction

Organic solar cells (OSCs) are a class of thin film solar cells that are fabricated from organic solids/polymers. OSCs offer advantages of fabrication into lightweight, plastic devices and large area modules [1] and easy integration in a wide variety of devices [2]. A small binding energy and a large diffusion length are advantageous in the performance of OSCs. This will allow excitons to reach the interface effectively and hence will lead to favorable dissociation of excitons into free charge carriers. The excitons in OSCs exist in singlet or triplet states which lead to different exciton binding energy (\(E_B\)), lifetime (\(\tau\)), diffusion coefficient (\(D\)) and diffusion length (\(L_D\)). In the case of OSCs, Frenkel excitons generally tend to have a high \(E_B\) due to small dielectric constant (\(\varepsilon\)), which is one of the major drawbacks as it makes the dissociation of excitons into the electron hole pairs (e-h), difficult. Also, \(L_D\) should be larger than or equal to the donor layer thickness for efficient exciton transport to the donor-acceptor interface.

In this paper, the roles of singlet and triplet excitons are discussed in view of optimizing the performance of OSCs. The main focus is placed on the exciton diffusion to the donor acceptor interface for effective dissociation. The excitonic Bohr radius and \(E_B\) for both singlet and triplet excitons are calculated and a comparison between the singlet and triplet exciton diffusion lengths, is presented using the Förster and Dexter transfers, respectively.

2 Exciton dynamics in OSCs

2.1 Exciton formation

In organic materials, \(\varepsilon\) is usually low (3-4) in comparison with inorganic semiconductors, for example, Silicon has \(\varepsilon=12\). Hence, \(E_B\) in OSCs is much larger than in inorganic solar cells. Upon illumination, both electron and hole (e-h) are excited on the same molecule of the donor and form a Frenkel exciton [3]. Electrons are excited to the lowest occupied molecular orbital (LUMO) leaving holes in the highest unoccupied molecular orbital (HOMO). Hence, the binding energy between a pair of excited e-h is given by

\[
E_B = \frac{k e^2}{\varepsilon r}
\]
where \( k = (4\pi e)^2 \times 8.9787 \times 10^9 \), \( e \) is the electronic charge and \( r \) is the average separation between the excited electron and hole. As an energy \( \geq E_g \) is required for effective dissociation of an exciton, it becomes more difficult to dissociate it into free e-h in organic solids. This is one of the main problems in achieving high efficiency in OSCs [4]. In an amorphous solid like one used for OSCs, the excitonic energies of singlet and triplet excitons are obtained as [5]:

\[
E(S = 0) = -\frac{(\alpha - 1)^2 \mu \epsilon e^2 k^2}{h^2},
\]

(2)

\[
E(S = 1) = -\frac{\mu \epsilon e^2 k^2}{2h^2},
\]

(3)

where \( S \) is the spin of an exciton (\( S = 0 \) for singlet and \( S = 1 \) for triplet), \( \alpha \) is a material dependent constant representing the ratio of the magnitude of the Coulomb and exchange interactions between the electron and hole in an exciton, \( \mu \) is the reduced mass of an exciton and \( h \) is the reduced Planck’s constant.

The excitonic Bohr radius is the separation between the electron and hole in an exciton and is also different for singlet and triplet excitons. The Bohr radii for singlet and triplet exciton diffusion, respectively, as [12]:

\[
a_x(S = 0) = \frac{\alpha^2 \mu \epsilon}{(\alpha - 1)^2 \mu \epsilon} a_0,
\]

(4)

\[
a_x(S = 1) = \frac{\mu \epsilon}{\mu \epsilon} a_0
\]

(5)

where \( a_0 = 5.29 \times 10^{-11} \text{ m} \) is the Bohr radius and \( \mu \) is the reduced mass of electron in hydrogen atom. \( E(S = 0, 1) \) and \( a_x(S = 0, 1) \) is calculated and compared in this paper.

### 2.2 Exciton diffusion

The two common exciton transfer mechanisms between the donor and acceptor materials are obtained through the Förster and Dexter transfer theories. They describe the transfer process of excitons as a function of the distance between the donor and acceptor materials [7]. The Förster and Dexter transfer processes are described below for the singlet and triplet exciton diffusion, respectively:

#### 2.2.1 Förster transfer

is a singlet to singlet energy transfer and is suitable for a long range process. It is a non-radiative, dipole-dipole (coulombic) interaction mechanism based on resonance theory of energy transfer and hence is also known as the fluorescent resonance energy transfer (FRET). In this process, a singlet exciton on a molecule in the donor gets deexcited and transports its energy to excite another singlet exciton on a different molecule. The rate of Förster transfer between donor and acceptor is given by [8]:

\[
k_f = \frac{1}{\tau} \left( \frac{R_f}{R_{da}} \right)^6
\]

(6)

where \( R_f \) is the Förster radius that determines the actual distance between the donor and acceptor, \( R_{da} \) is the donor-acceptor materials separation distance and \( \tau \) is the lifetime.

If \( R_f = R_{da} \) one gets an efficiency of 50% for the Förster’s transfer.

#### 2.2.2 Dexter transfer

The theory of resonance energy transfer was subsequently extended by Dexter to triplet excitons with electric dipole-forbidden transitions [9]. The nearest neighbor diffusion of charge carriers is enabled through the electron exchange interaction between triplet excitons. This is a very short range process since it requires the overlap of the electronic wavefunctions of two molecules. It is also a non-radiative energy transfer by exchange interaction. The Dexter rate of transfer is given by [8]:

\[
k_d = \frac{1}{\tau} \exp \left[ \frac{2R_d}{L} \left( 1 - \frac{R_{da}}{R_d} \right) \right]
\]

(7)

where \( L \) is the average length of a molecular orbital and \( R_d \) is the Dexter radius between donor and acceptor at which the efficiency of such transfer remains at 50% [7].

### 3 Results

#### 3.1 Excitonic binding energy and Bohr radius

The exchange energy (\( \Delta E_{ex} \)) between singlet and triplet is (2)-3) and is obtained as:

\[
\Delta E_{ex} = 1 - \left( \frac{(\alpha - 1)^2 \mu \epsilon e^2 k^2}{2h^2} \right)
\]

(8)

In conjugated polymers, the measured value of \( \Delta E_{ex} \) is about 0.7 eV [10]. In organic polymers, the effective masses of electrons and holes are not expected to be very different from the free electron mass, \( m_e \), hence it is assumed that \( m_e = m_h = m_o \), giving \( \mu = 0.5m_o \) [11]. Using \( \epsilon = 3 \), we get \( \alpha = 1.37 \) from Eq. (8) and using these values in Eqs. (2) and (3), one gets singlet and triplet excitonic binding energies, respectively, as \( E_b(S) = E(S) \). The excitonic Bohr radius for singlet and triplet excitons is calculated using Eqs. (4) and (5), respectively. The values of binding energies and Bohr radii, thus calculated, are listed in Table 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Singlet (S=0)</th>
<th>Triplet (S=1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy ( \Delta E(S) ) (eV)</td>
<td>0.059</td>
<td>0.759</td>
</tr>
<tr>
<td>Excitonic Bohr radius ( a_x(S) ) (nm)</td>
<td>4.352</td>
<td>0.317</td>
</tr>
</tbody>
</table>

#### 3.2 Diffusion coefficient and excitonic diffusion length

The diffusion coefficient, \( D \), is the ratio of the exciton diffusion to its lifetime and can be determined for singlet and triplet excitons using the Förster and Dexter transfer, respectively as [12]:

\[
D(S) = \frac{R_f^6}{6 \pi \alpha^4}, \quad \text{for singlet excitons and}
\]

(9)

\[
D(T) = \frac{R_d^2}{6 \pi} \exp \left[ \frac{2R_d}{L} \left( 1 - \frac{R_{da}}{R_d} \right) \right], \quad \text{for triplet excitons}
\]

(10)

where \( S \) denotes singlet state and \( T \) denotes triplet state.
The relationship between \( D(T) \) and \( D(S) \) using Eqs. (9) and (10) is obtained as:

\[
D(T) = \frac{R_f^2 R_{da}^4}{R_f^6} \exp \left[ \frac{2 R_f}{L} \left( 1 - \frac{R_{da}}{R_d} \right) \right] D(S)
\]

The diffusion length, \( L_D \), for singlet and triplet excitons are dependent on the Förster and Dexter rates, respectively. The singlet \( L_D(S) \) and triplet \( L_D(T) \) diffusion lengths are obtained as:

\[
L_D(S) = \frac{1}{\sqrt{6}} \frac{R_f}{R_d}
\]

\[
L_D(T) = \frac{R_{da}}{\sqrt{6}} \exp \left[ \frac{R_d}{L} \left( 1 - \frac{R_{da}}{R_d} \right) \right]
\]

Using Eqs. (11) and (12), we get the relation between singlet-triplet diffusion lengths as

\[
L_D(T) = \left( \frac{R_d}{R_f} \right)^3 \exp \left[ \frac{R_f}{L} \left( 1 - \frac{R_{da}}{R_d} \right) \right] L_D(S)
\]

The values of \( R_f \), \( R_d \) and \( \tau \) for various organic materials in their singlet and triplet states are listed in Table 2.

**Table 2** Values of \( R_f \), \( R_d \) and \( \tau \) for various organic materials as used in the calculations.

<table>
<thead>
<tr>
<th>Organic Material</th>
<th>Singlet (S)/Triplet (T)</th>
<th>( R_f ) or ( R_d ) (Å)</th>
<th>( \tau ) (ns)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPD</td>
<td>S</td>
<td>19.0</td>
<td>3.5</td>
<td>[12]</td>
</tr>
<tr>
<td>CBP</td>
<td>S</td>
<td>22.0</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>SubPc</td>
<td>S</td>
<td>15.0</td>
<td>≤1</td>
<td></td>
</tr>
<tr>
<td>PTCDA</td>
<td>S</td>
<td>14.0</td>
<td>3.2 (±0.7)</td>
<td></td>
</tr>
<tr>
<td>DIP</td>
<td>S</td>
<td>17.0</td>
<td>1.8 (±0.5)</td>
<td></td>
</tr>
<tr>
<td>PeEOP</td>
<td>T</td>
<td>0.7</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>Meo-POV</td>
<td>S</td>
<td>19.0</td>
<td>0.055</td>
<td>[13]</td>
</tr>
<tr>
<td>PDHFV</td>
<td>S</td>
<td>22.0</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>PTEH</td>
<td>S</td>
<td>24.0</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>PDHFHPPV</td>
<td>S</td>
<td>43.0</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>Ir(ppy)$_3$</td>
<td>S</td>
<td>35.8</td>
<td>1330</td>
<td>[7]</td>
</tr>
<tr>
<td>in PMMA</td>
<td>T</td>
<td>10.5</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>Nile Red/PCBM</td>
<td>S</td>
<td>27.0</td>
<td>-</td>
<td>[14]</td>
</tr>
<tr>
<td>Ir(ppy)$_3$/PVK</td>
<td>S</td>
<td>31.7</td>
<td>-</td>
<td>[15]</td>
</tr>
<tr>
<td>Ir(ppy)$_3$/PFHP</td>
<td>S</td>
<td>30.7</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Using the parameters listed in Table 2, \( D \) from Eq. (9) and (10) are calculated and plotted as a function of donor-acceptor separation for PDHFHPPV, PDHFV, Ir(ppy)$_3$ in PMMA and Meo-POV in Fig. 1. The other polymers listed in Table 2 show similar behavior as Meo-POV and hence have not been shown in the figure.

**Figure 1** Diffusion coefficient for singlet (S) and triplet (T) states for organic materials plotted as a function of \( R_{da} \).

Figure 1 shows that for \( R_{da} \) at 0.05 nm, PDHFHPPV has the highest \( D \) of singlet excitons followed by PDHFV and Meo-POV. Using Eqs. (12) and (13), the diffusion lengths for the Förster and Dexter rates are calculated and plotted in Fig. 2 for PDHFHPPV, Ir(ppy)$_3$ in PMMA, PDHFV and Ir(ppy)$_3$/PVK. The other polymers listed in Table 2 show similar behavior as PDHFV and hence have not been shown in the plot. The highest \( L_D = 3.25 \times 10^3 \) nm was for PDHFHPPV.

**Figure 2** Exciton diffusion lengths for singlet (S) and triplet (T) excitons in various organic materials versus \( R_{da} \).

4 Discussion A comprehensive study of exciton binding energies, lifetimes, diffusion coefficients and diffusion lengths for the singlet and triplet excitons have been presented. The triplet binding energy is about an order of magnitude greater than that of singlet while the singlet excitonic Bohr radius is an order, greater than that of triplet. In OSCs, the difference in the energy levels between the donor and acceptor contributes to exciton dissociation. Scharber et al. [16] have shown that the energy required to dissociate excitons is \( \Delta E = LUMO_T - LUMO_D = 0.3 \) eV, which is sufficient for charge separation, providing an efficiency.
of 10% in single bulk-heterojunction solar cells. This also agrees with Koster et al. [17], that a more efficient charge separation is achieved when donor-acceptor offset is about 0.4 eV. The underlying condition is \( AE \gtrsim ES \) in order to effectively dissociate Frenkel excitons into free e-h. The condition is satisfied only in the case of singlet excitons which has \( ES(S=0) = 0.059 \text{ eV} \). The excitonic binding energy for triplet state \( ES(S=1) = 0.755 \text{ eV} \), which is more than double the LUMO offset. This implies that it is easier to dissociate singlet excitons than triplet excitons. Hence for dissociation of excitons into free e-h, excitation to singlet state is favored over the triplet state.

Furthermore at LUMO offset=0.3 eV, the separation (r) between electron and hole in an exciton should be 1.6 nm (calculated from Eq. (1)), to dissociate it into free e-h pairs. Both the singlet and triplet exciton Bohr radii appear to be large enough for effective dissociation of excitons. As the singlet excitonic Bohr radius of \( a_s(S = 0) = 4.352 \text{ nm} \) is an order of magnitude greater than that of triplet exciton, it maybe concluded that singlet excitons are dissociated more easily than triplet.

Most organic polymers show similar D with respect to \( R_{da} \) as shown in Fig. 1. Lower D is found in most polymers except for PDHF1HPPV and PDHFV. This may be attributed to the low values of \( E_b \) and singlet excitons which has \( ES(S=0) = 0.059 \text{ eV} \). The excitonic binding energy for triplet state \( ES(S=1) = 0.755 \text{ eV} \), which is more than double the LUMO offset. This implies that it is easier to dissociate singlet excitons than triplet excitons. Hence for dissociation of excitons into free e-h, excitation to singlet state is favored over the triplet state.

As shown in Fig. 2, \( L_D \) for all organic materials show similar decrease at larger \( R_{da} \) and it eventually becomes a minimum at \( R_{da} > 1.5 \text{ nm} \) for all materials, \( L_{D}(S) > L_{D}(T) \). At 1.5 nm, Ir(ppy)_3 has \( L_{D}(S) = 8.32 \text{ nm} \) and \( L_{D}(T) \) is only, \( 1.02 \times 10^{-2} \text{ nm} \). In this case, \( L_{D}(S) \) is around two orders of magnitude larger than \( L_{D}(T) \). Both diffusion lengths, singlet and triplets have significant values for \( R_{da} < 1.5 \text{ nm} \) but reduce to zero as the separation increases.

5 Conclusions The effects of binding energy, excitonic Bohr radius, diffusion coefficient and diffusion length on the dissociation of singlet and triplet states are investigated. It is found that singlet excitons dissociate more easily than triplet excitons because of low \( E_b \) and large \( a_s \). The Förster and Dexter models are used to study the singlet and triplet diffusion coefficients and diffusion lengths, respectively. The singlet exciton diffusion length is larger than that of triplets at small separation between the donor and acceptor which is attributed to its large diffusion coefficient. On the basis of this study, one may conclude that diffusion and dissociation of singlet excitons occurs more easily than triplet excitons.

References