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# 1 Photovoltaic Contribution of Photo-generated Excitons in Acceptor 2 Material of Organic Solar Cells

3  
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9  
10 **Abstract** Contribution of exciton generation in acceptor material to the photovoltaic performance of  
11 three bulk-heterojunction organic solar cells (BHJ OSCs), PTB7:PC<sub>71</sub>BM, P3HT:ICBA and  
12 P3HT:PC<sub>61</sub>BM are studied. Singlet and triplet rates of absorption and dissociation and diffusion  
13 lengths are calculated and compared with those when excitons are generated in the donor of these  
14 BHJ OSCs. It is found that the rates of absorption and dissociation and diffusion lengths are  
15 comparable whether excitons are generated in donor or acceptor of these BHJ OSCs. Therefore, it is  
16 proposed that the contribution of exciton generation in acceptor may not be negligible.

## 17 18 **1 Introduction**

19  
20 Research interests in organic solar cells (OSCs) have escalated over the past few decades due to their  
21 cost effectiveness, flexibility, easy fabrication techniques and large scale production [1-5]. In bulk-  
22 heterojunction (BHJ) OSCs, the donor and acceptor materials are blended together to form the organic  
23 active layer [6]. The principle processes of operation of BHJ OSCs include: 1) Photon absorption and  
24 exciton formation [7,8], 2) exciton diffusion to the donor-acceptor (D-A) interface [9,10], 3) exciton  
25 dissociation at the interface [11,12] and 4) transport and collection of free charge carriers at their  
26 respective electrodes.

27 The excited excitons, either in the donor or acceptor material, diffuse to the D-A interface and  
28 then form charge transfer (CT) excitons, which have their electrons in the acceptor and holes in the  
29 donor, before dissociating into free electrons and holes which are drawn to cathode and anode,  
30 respectively [13-15]. The photon absorption can occur in both donor and acceptor materials of BHJ  
31 OSCs as already known [16-20] but the mechanism of dissociation of excitons excited in the acceptor  
32 material and their contribution to the power conversion efficiency of BHJ OSCs has not been fully  
33 understood. Pettersson et al. [21] have shown that the photocurrent generated by the absorption in the  
34 acceptor fullerene needs to be taken into account to get an accurate modelling of the photocurrent  
35 action spectra in a bilayer OSC of polymer/fullerene. Liang et al. [22] have measured the absorption  
36 of photons in both, the donor benzodithiophene polymers (PTB7) and acceptor phenyl-C<sub>71</sub>-butyric

1 acid methyl ester (PC<sub>71</sub>BM). According to their study, the acceptor, PC<sub>71</sub>BM compensates the  
2 absorption in the visible region where the donor's absorption is weak and thus the combined  
3 absorption in both contributes to the total conversion efficiency of 7.4%. Furthermore, using the time-  
4 resolved spectroscopy, Yonezawa et al. [23] have measured the free carrier-formation times from  
5 excitons in PTB7 and PC<sub>71</sub>BM and found they are nearly the same as 0.35 ps and 0.21 ps,  
6 respectively.

7 Furthermore, in a study carried out by Dastoor et al. [24], at almost all excitation wavelengths,  
8 they have observed that more light is absorbed by the acceptor in the 1:4 polymer (donor):fullerene  
9 (acceptor) blends than is absorbed by the polymer (donor) and the fullerene component contributed  
10 over half of the total generated photocurrent. Nicolaidis et al. [25] have modelled 1:1 blend of poly (3-  
11 hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) devices and found  
12 that the fullerene component contributes almost 13% of the total photocurrent generated in the  
13 devices.

14 Mihailetchi et al. [26] have considered the generation of CT excitons at the D-A interface by  
15 photon absorption in either donor or acceptor material and calculated the rate of exciton dissociation  
16 using Braun's model [24] developed on the basis of Onsager's theory. However, to the best of our  
17 knowledge, no report has yet been published that clearly demonstrates how a charge-transfer exciton  
18 gets dissociated at the D-A interface. In other words, where does the excess energy equivalent to at  
19 least the binding energy of the CT exciton comes from to dissociate it? On one hand, a CT exciton  
20 having its excited electron and hole on different but neighbouring molecules may be expected to have  
21 a larger exciton Bohr radius than a Frenkel exciton (electron and hole being on the same molecule).  
22 Thus, a CT exciton may be regarded to have a lower binding energy and hence easier to dissociate.  
23 On the other hand, in a BHJ OSC, both donor and acceptor materials are organic and hence are  
24 expected to have similar dielectric constants. That means a CT exciton's binding energy is not  
25 negligible and it may not automatically dissociate into a pair of free electron and hole at the D-A  
26 interface.

27 Recently, we have modelled [27] the dissociation of a CT exciton at the D-A interface formed  
28 through a Frenkel exciton excited in the donor as a two-step process: First, a Frenkel exciton in the  
29 donor transfers its electron to an acceptor molecule across the interface which has a lower LUMO  
30 energy and then the excess energy equal to the difference in energy between the donor and acceptor  
31 LUMOs is released in the form of molecular vibrational energy. This energy may impact back on to  
32 the CT exciton and if it is equal to or more than the binding energy of the CT exciton it will dissociate  
33 it into free electron and hole.

34 The aim of this paper is to study the absorption of photons in the acceptor material of BHJ OSCs  
35 and similar to the dissociation of donor excitons, propose a model for the mechanism of dissociation  
36 of excitons excited in the acceptor. The rate of dissociation of such excitons is calculated and its  
37 contribution to the photovoltaic performance of BHJ OSCs is estimated. Here also the mechanism of

1 dissociation is considered as a two-step process: First, when an exciton excited in the acceptor reaches  
 2 the D-A interface, the hole gets transferred to the donor's highest occupied molecular orbital (HOMO)  
 3 which is at a lower energy and thus a CT exciton is formed with the hole in the donor and electron in  
 4 the acceptor. In the second step, the excess energy equivalent to the energy difference between the  
 5 HOMOs of acceptor and donor released as molecular vibrational energy, if at least equal to the CT  
 6 exciton binding energy, impacts on the CT exciton and dissociates it. The derived rate for the  
 7 dissociation is general and can be applied to any donor/acceptor blend by using the relevant material  
 8 parameters.

## 10 **2 Methodology**

12 As stated above, here we have proposed a two-step mechanism for the dissociation of excitons excited  
 13 in the acceptor of a BHJ OSC. When photons are absorbed in the acceptor, electrons (e) are excited  
 14 from the acceptor's HOMO to its lowest unoccupied molecular orbital (LUMO) by creating holes (h)  
 15 in the HOMO. These excited pairs of e and h instantly form Frenkel excitons in the acceptor, then, as  
 16 stated above, diffuse within the acceptor and when they reach the donor-acceptor interface, the hole  
 17 gets transferred from the acceptor's HOMO to the donor's HOMO because donor's HOMO lies at a  
 18 lower hole energy, leading to CT excitons formed at the interface. The excess energy equivalent to the  
 19 donor's and acceptor's HOMO offset ( $\Delta E = E_{HOMO}^D - E_{HOMO}^A$ ) is released as the molecular  
 20 vibrational energy. If  $\Delta E \geq E_B$ , the exciton binding energy, then the released molecular vibrational  
 21 energy may impact back and dissociate the CT excitons into free e and h pairs, which are collected at  
 22 the opposite electrodes and hence may contribute to the photovoltaic current. The derivation of the  
 23 rates of such absorption and dissociation is based on our recent works for the absorption and  
 24 dissociation of excitons excited in the donor material [27] of BHJ OSCs.

25 The photons absorbed in the acceptor lead to the excitation of Frenkel excitons in either singlet  
 26 (S) or triplet (T) state. The binding energies of singlet and triplet excitons are obtained as

$$27 \quad E_B^S = -\frac{(\alpha-1)^2 \mu_x e^4 k^2}{\alpha^2 2\hbar^2 \varepsilon^2} = 0.06 \text{ eV} \quad \text{and} \quad E_B^T = -\frac{\mu_x e^4 k^2}{2\hbar^2 \varepsilon^2} = 0.76 \text{ eV}, \text{ respectively [10], where}$$

28  $k = (4\pi\varepsilon_0)^{-1} = 9 \times 10^9$ ,  $e$  is the electronic charge,  $\mu_x$  is the reduced mass of an exciton,  $\hbar$  is the  
 29 reduced Planck's constant,  $\varepsilon$  is the dielectric constant and  $\alpha$  is a material dependent constant  
 30 representing the ratio of the magnitude of the Coulomb and exchange interactions between the  
 31 electron and hole in an exciton. Following our earlier work [7], the rates of photon absorption for a  
 32 singlet excitation due to exciton-photon interaction ( $R_A^S$ ) and triplet excitation due to exciton-spin-  
 33 orbit-photon interaction ( $R_A^T$ ), respectively, in the acceptor can be obtained as:

$$1 \quad R_A^S = \frac{4ke^2(E_{LUMO}^A - E_{HOMO}^A)^3 a_{xs}^2}{3c^3 \epsilon^{1.5} h^4} \quad (1)$$

$$2 \quad R_A^T = \frac{32e^6 Z^2 k^2 \epsilon (E_{LUMO}^A - E_{HOMO}^A)}{c^7 \epsilon_o \mu_x^4 a_{xt}^4} \quad (2)$$

3 where  $(E_{LUMO}^A - E_{HOMO}^A)$  is the bandgap of the acceptor,  $a_x$  is the excitonic Bohr radius,  $c$  is the  
4 speed of light,  $\epsilon_o$  is the vacuum permittivity and  $Z$  is the highest atomic number in a molecule [7].

5 After excitation, the singlet excitons diffuse through the acceptor to the donor-acceptor  
6 interface either via Förster resonance transfer or Dexter transfer and the triplet exciton diffuses  
7 through the Dexter transfer mechanism. It may be noted that an exciton is an electrically neutral entity  
8 and hence cannot be directed to move in any particular direction by any kind of built-in electric fields  
9 in the material. The diffusion lengths for singlet ( $L_D^S$ ) and triplet excitons ( $L_D^T$ ) are obtained as [10]:

$$10 \quad L_D^S = \frac{R_f^3}{\sqrt{6} R_{da}^2} \quad (3)$$

$$11 \quad L_D^T = \frac{R_{da}}{\sqrt{6}} \exp\left[\frac{R_d}{L} \left(1 - \frac{R_{da}}{R_d}\right)\right] \quad (4)$$

12 where  $R_f$  and  $R_d$  are the Förster and Dexter radii, respectively,  $R_{da}$  is the donor-acceptor separation  
13 distance and  $L$  is the average length of the associated molecular orbital.

14 At the interface, a Frenkel exciton created in the acceptor relaxes to a CT exciton by  
15 transferring the hole from the HOMO of the acceptor to the HOMO of the donor, releasing the excess  
16 energy to molecular vibrations. This occurs because the HOMO of acceptor lies lower than that of the  
17 donor which is energetically favourable for holes. This molecular vibrational energy, if equal or  
18 greater than the binding energies of singlet ( $E_B^S$ ) and triplet ( $E_B^T$ ) excitons may dissociate the singlet  
19 and triplet CT excitons into free charge carriers. We have described briefly the derivation of rate of  
20 dissociation here however for details one may refer to our earlier paper [27].

21 It is considered that the transition from a CT exciton to free charge carriers occurs due to the  
22 exciton molecular vibration interaction operator,  $\hat{H}_d$  derived as [27]:

$$23 \quad \hat{H}_d = \sum_{n=1}^N \sum_{v=1}^n \hbar \omega_v G_v B_n^+(S) B_n(S) (b_{nv}^+ + b_{nv}) \quad (5)$$

24 where  $\omega_v$  is the molecular vibration frequency and  $b_{nv}^+$  ( $b_{nv}$ ) is the phonon creation (annihilation)  
25 operator in the vibrational mode,  $v$  and  $N$  is the number of molecules.  $G_v$  is the exciton-phonon  
26 coupling constant, which is a dimensionless parameter representing the linear displacement in the  
27 excited state of a molecule associated with the vibrational mode,  $v$  and is given by:

$$G_v = \sqrt{\frac{M_{eff} \omega_v}{2\hbar}} (q_{vo} - q_{oo}) \quad (6)$$

where  $M_{eff}$  is the effective nuclear mass (atomic mass of a nucleus in a molecule),  $q_{vo}$  denotes the displacement associated with the vibrational mode  $v$  by which a molecule gets shifted when excited from HOMO to LUMO and  $q_{oo}$  is the equilibrium position in the ground state along the dimensionless coordinate,  $\lambda$ , which is given by  $\lambda = (q_{vo} - q_{oo})\sqrt{M_{eff} \omega / 2\hbar}$  [25].  $B_n^+(S)$  and  $B_n(S)$  are the exciton creation and annihilation operators, respectively, with spin  $S = 0$  for a singlet or 1 for a triplet exciton.

The dissociation occurs due to the transition from an initial state  $|i\rangle$  consisting of a CT exciton and molecular vibrations to a final state  $|f\rangle$  of dissociated free electron and hole and molecular vibrations. Thus, the initial and final states can be respectively written as [27]:

$$|i\rangle = N^{-1} \sum_n B_n^+(S) b_{nv}^+ |0; v\rangle, \quad (7)$$

and

$$|f\rangle = N^{-3/2} \sum_{l_1, m_1} \sum_{\sigma'_e, \sigma'_h, v_1} a_{l_1, l_1}^+ (\sigma'_e) d_{m_1, H_1}^+ (\sigma'_h) |0; v_1\rangle \quad (8)$$

where  $|0; v\rangle = |0\rangle|v\rangle$ , where  $|0\rangle$  represents the electronic vacuum state with the LUMO completely empty and HOMO completely full and  $|v\rangle$  represents the occupation of the vibrational state. Expanding the exciton operator in Eq. (7) in terms of electron and hole operators and using Eqs (5) – (8), the transition matrix element is obtained as [27]:

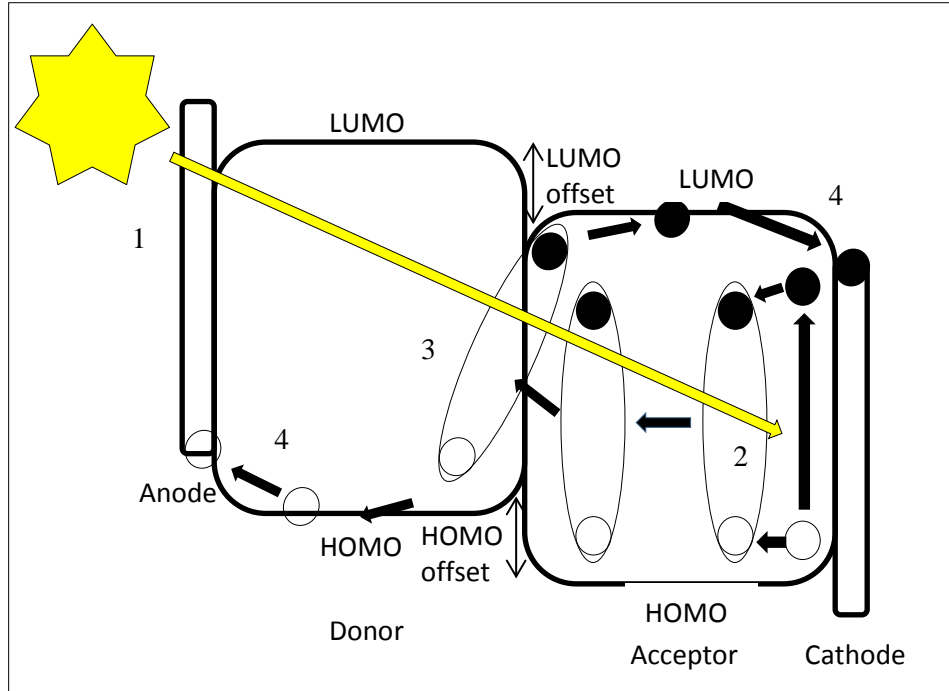
$$\langle f | H_d | i \rangle = \frac{N^{-1}}{(4\pi)^2} \sum_n \hbar \omega_{nv} G_v n_v \quad (9)$$

where  $n_v$  is the number of phonons (number of quanta of molecular vibrational energy) required to dissociate a CT exciton. It may be reminded here again that the transition matrix element is obtained from a two-step process: 1) a Frenkel exciton becomes a CT exciton by transferring the hole to a donor molecule and 2) the excess molecular vibrational energy is given to the CT exciton to dissociate it. At any point in the sample, both CT exciton and molecular vibrational energy can be transferred in any direction of a solid angle of  $4\pi$ . Therefore, as explained in [27], the probability of transferring each in any particular direction becomes  $(4\pi)^{-1}$ . This is the reason that the transition matrix element is divided by  $(4\pi)^2$ .

Using Fermi's golden rule and the transition matrix element in Eq. (9), rate of dissociation of an exciton created in the acceptor can be written as [27]:

$$R_D^i = \frac{8\pi^2}{3(4\pi)^4 \hbar^3 \epsilon^2 E_B^i} [(E_{HOMO}^A - E_{HOMO}^D) - E_B^i]^2 (\hbar\omega_v) \mu_x a_{xi}^2, \quad (10)$$

where the rate in Eq. (10) is applicable to a singlet or triplet exciton by substituting  $i = S$  or  $T$  and using the corresponding material parameters. It may be noted that the rate in Eq. (10) is non-zero only for  $(E_{HOMO}^A - E_{HOMO}^D) \geq E_B^i$ . After the dissociation, the electron moves to the cathode and the hole towards the anode with the aid of the workfunction difference between the two electrodes [11]. The process of dissociation of excitons created in the acceptor is illustrated in Fig. 1.



**Figure 1** 1. Photon absorption, 2. exciton diffusion, 3. dissociation of excitons generated in the acceptor and 4. charge carrier collection at electrodes in a bulk-heterojunction OSC.

### 3 Results and Discussions

The rates of photon absorption in singlet and triplet states, exciton diffusion lengths and exciton dissociation rates for three BHJ OSCs: PTB7:PC<sub>71</sub>BM (1:1.5) [28], P3HT:indene-C<sub>60</sub> bisadduct (ICBA) (1:1) [29,30] and P3HT:PC<sub>61</sub>BM (1:1) [31,32]. Although, the highest power conversion efficiency achieved for OSCs to-date has exceeded 11% [5], a PTB7:PC<sub>71</sub>BM based BHJ OSC has exhibited the highest power conversion efficiency ( $\eta$ ) of 9.2% [28], and another combination of P3HT and ICBA has produced  $\eta=6.5\%$  [30], where the acceptor, ICBA, has been found to possess better solubility in organic solvents and a stronger visible absorption than PCBM [33].



To investigate the effect of different fullerene derivatives in acceptor materials, ICBA and PC<sub>61</sub>BM were chosen and their rates of absorption, diffusion lengths and rates of dissociation were compared, while using the same donor material, P3HT in the two BHJ OSCs. The input parameters used for calculating the diffusion lengths, rates of absorption and dissociation of singlet and triplet excitons in the above three BHJ OSCs are shown in Table 1. The rates of photon absorption in singlet and triplet states, exciton diffusion lengths and exciton dissociation rates for three BHJ OSCs are calculated as listed in Table 2.

**Table 1** Input parameters for donor and acceptor materials for PTB7:PC<sub>71</sub>BM, P3HT:ICBA and P3HT:PC<sub>61</sub>BM BHJ OSCs

Parameter	Value	Reference
singlet exciton Bohr radius, $a_{xs}$	4.35 nm	[10]
triplet exciton Bohr radius, $a_{xT}$	0.317 nm	
$R_{da}$	0.05 nm	
$L$	0.11 nm	
$\epsilon_{polymer}$ ; $\epsilon_{fullerene}$	3 – 4; 4.4	[34,35]
PTB7:PC <sub>71</sub> BM		
$E_{HOMO}^{PTB7}$ ; $E_{LUMO}^{PTB7}$	5.15 eV; 3.31 eV	[28]
$E_{HOMO}^{PC_{71}BM}$ ; $E_{LUMO}^{PC_{71}BM}$	6.10 eV; 4.30 eV	
Förster radius, $R_f^{PTB7}$	2.17 nm	[36,37]
Dexter radius, $R_d^{PTB7}$	0.75 nm	
$R_f^{PC_{71}BM}$ ; $R_d^{PC_{71}BM}$	3.10 nm; 0.60 nm	[38]
P3HT:ICBA		
$E_{HOMO}^{P3HT}$ ; $E_{LUMO}^{P3HT}$	5 eV; 3 eV	[32,39]
$E_{HOMO}^{ICBA}$ ; $E_{LUMO}^{ICBA}$	6 eV; 4 eV	
$R_f^{P3HT}$ ; $R_d^{P3HT}$	8 nm; 1 nm	[40]
$R_f^{ICBA}$ ; $R_d^{ICBA}$	3.30 nm; 0.70 nm	[41,42]
P3HT:PC <sub>61</sub> BM		
$E_{HOMO}^{PC_{61}BM}$ ; $E_{LUMO}^{PC_{61}BM}$	6.1 eV; 3.7 eV	[43]
$R_f^{PC_{61}BM}$ ; $R_d^{PC_{61}BM}$	2.4 nm; 0.60 nm	[38,44]

**Table 2** Calculated rates of absorption using Eqs. (1) and (2) and dissociation using Eq. (10), and diffusion lengths using Eqs. (3) and (4) for singlet and triplet excitons excited in the acceptor of PTB7:PC<sub>71</sub>BM, P3HT:ICBA and P3HT:PC<sub>61</sub>BM based BHJ OSCs.

Donor: Acceptor	Absorption Rates		Diffusion Lengths		Dissociation Rates	
	$R_A^S$ (s <sup>-1</sup> )	$R_A^T$ (s <sup>-1</sup> )	$L_D^S$ (m)	$L_D^T$ (m)	$R_D^S$ (s <sup>-1</sup> )	$R_D^T$ (s <sup>-1</sup> )
PTB7:PC <sub>71</sub> BM	4.46×10 <sup>9</sup>	2.40×10 <sup>7</sup>	4.86×10 <sup>-6</sup>	3.03×10 <sup>-9</sup>	1.30×10 <sup>14</sup>	2.49×10 <sup>9</sup>
P3HT:ICBA	5.50×10 <sup>9</sup>	2.96×10 <sup>7</sup>	5.87×10 <sup>-6</sup>	7.52×10 <sup>-9</sup>	1.52×10 <sup>14</sup>	4.17×10 <sup>9</sup>
P3HT:PC <sub>61</sub> BM	6.12×10 <sup>9</sup>	3.29×10 <sup>7</sup>	2.26×10 <sup>-6</sup>	3.03×10 <sup>-9</sup>	2.05×10 <sup>14</sup>	9.19×10 <sup>9</sup>

1 In the case of a PTB7:PC<sub>71</sub>BM BHJ OSC, the HOMO offset between PTB7 and PC<sub>71</sub>BM is  
2 0.95 eV, which is sufficient to dissociate both singlet and triplet CT excitons at the interface.  
3 Likewise, in P3HT:ICBA and P3HT:PC<sub>61</sub>BM BHJ OSCs, the HOMO offsets are 1.00 eV and 1.10  
4 eV, respectively, which are also adequate for dissociating both singlet and triplet CT excitons at the  
5 interface. For ICBA and PC<sub>61</sub>BM fullerene derivatives, rates of absorption and dissociation in  
6 PC<sub>61</sub>BM was slightly higher than ICBA, which may be attributed to higher energy gap and HOMO  
7 offset, respectively. Similar behaviour was observed in their exciton diffusion lengths, hence it can be  
8 noted that PC<sub>61</sub>BM is a better acceptor than ICBA.

9 According to Table 2, the rate of absorption for singlet excitons is mostly around two orders  
10 of magnitude higher than that in triplet excitons in the BHJ OSCs considered here. This may be  
11 attributed to the fact that  $R_A^S$  depends on  $(E_{HOMO} - E_{LUMO})^3$  while  $R_A^T$  is linearly dependent on  
12  $(E_{HOMO} - E_{LUMO})$ . In all three OSCs, the singlet exciton diffusion length is about three orders of  
13 magnitude greater than the triplet exciton diffusion length as obtained by the Förster and Dexter  
14 transfer mechanisms. The experimental value for singlet excitonic diffusion lengths for PC<sub>61</sub>BM and  
15 pure ICBA are 5 nm [45] and 40 nm [46], respectively, which are about two to three orders of  
16 magnitude greater than their calculated values in Table 2. Also, the calculated rate of dissociation of  
17 singlet excitons ( $R_D^S$ ) is found to be  $1 - 3.3 \times 10^{14} \text{ s}^{-1}$ , which gives a dissociation time of 4 – 6 fs. This  
18 is in reasonable agreement with the experimentally measured forward transfer time (CT exciton  
19 formation time) of 45 fs by Brabec et al. [47].

20 The calculated  $R_D^S$  is about five orders of magnitude greater than  $R_D^T$  in PTB7:PC<sub>71</sub>BM,  
21 P3HT:ICBA and P3HT:PC<sub>61</sub>BM BHJ OSCs. As the diffusion length and rate of dissociation of  
22 singlet excitons are found to be higher (Table 2), one may conclude that in these three BHJ OSCs, the  
23 creation of singlet excitons may be regarded to be of better photovoltaic advantage than triplet  
24 excitons. However, the diffusion lengths in some other combination of BHJ OSCs are found to be of  
25 similar magnitude for both singlet and triplet excitons [9,48].

26 Based on the above analysis, it may be concluded that the excitation of excitons in the  
27 acceptor material does contribute to the photovoltaic conversion efficiency in BHJ OSCs as has been  
28 found in previous reports as well [21,22,24,25]. For a comparative study, we have also calculated the  
29 rates of absorption and dissociation, and diffusion lengths in the three BHJ OSCs when the excitons  
30 are generated in the donor material and listed in Table 3.

31

1 **Table 3** Calculated rates of singlet and triplet absorption and dissociation and diffusion lengths for  
 2 excitations in the donor of PTB7:PC<sub>71</sub>BM, P3HT:ICBA and P3HT:PC<sub>61</sub>BM BHJ OSCs.

Donor:Acceptor	Absorption Rates		Diffusion Lengths		Dissociation Rates	
	$R_A^S$ (s <sup>-1</sup> )	$R_A^T$ (s <sup>-1</sup> )	$L_D^S$ (m)	$L_D^T$ (m)	$R_D^S$ (s <sup>-1</sup> )	$R_D^T$ (s <sup>-1</sup> )
PTB7:PC <sub>71</sub> BM	$8.47 \times 10^9$	$4.55 \times 10^7$	$1.67 \times 10^{-6}$	$1.18 \times 10^{-8}$	$3.18 \times 10^{14}$	$8.17 \times 10^9$
P3HT:ICBA	$1.09 \times 10^{10}$	$5.84 \times 10^7$	$8.36 \times 10^{-5}$	$1.15 \times 10^{-7}$	$3.28 \times 10^{14}$	$8.98 \times 10^9$
P3HT:PC <sub>61</sub> BM	$1.09 \times 10^{10}$	$5.84 \times 10^7$	$8.36 \times 10^{-5}$	$1.15 \times 10^{-7}$	$1.06 \times 10^{14}$	$3.77 \times 10^8$

3  
 4 For PTB7:PC<sub>71</sub>BM BHJ OSC, the singlet and triplet absorption rates in PTB7 donor and  
 5 PC<sub>71</sub>BM acceptor are of the same order. However, the singlet absorption rates for excitation in P3HT  
 6 are an order of magnitude greater than the fullerene derivatives as shown in Tables 2 and 3. This may  
 7 be attributed to the fact that the  $\epsilon$  in P3HT is lower and in fullerene derivatives [49].

8 The singlet and triplet diffusion lengths are about an order of magnitude larger when  
 9 excitation occurs in the donor as compared to the acceptor. Finally for dissociation, the LUMO offset  
 10 is sufficient to overcome the singlet and triplet binding energies and hence both CT excitons may  
 11 dissociate efficiently into free charge carriers in the OSCs. Excitation in either donor or acceptor  
 12 produces the same rate of singlet exciton dissociation in OSCs, however, the rate of triplet exciton  
 13 dissociation in P3HT:PC<sub>61</sub>BM is an order of magnitude lower than other two BHJ OSCs because its  
 14 LUMO offset is lower.

15 Overall, most excitonic processes are comparable in magnitude when excitation occurs in  
 16 donors or in acceptors in PTB7:PC<sub>71</sub>BM, P3HT:ICBA and P3HT:PC<sub>61</sub>BM BHJ OSCs. Excitations  
 17 either in the donor or acceptor produce high rates of exciton absorption and dissociation and also  
 18 comparable diffusion lengths so that singlet and triplet excitons could reach the donor-acceptor  
 19 interface readily. The higher power conversion efficiency observed in the above BHJ OSCs may thus  
 20 be attributed to the photovoltaic contributions from both donors and acceptors.

## 21 22 **4 Conclusions**

23  
 24 The contribution of excitons excited in the acceptor material to the photovoltaic performance of BHJ  
 25 OSCs is calculated and compared with that when excitons are generated in the donor material. Most  
 26 of the properties, including the rates of absorption and dissociation and diffusion lengths for singlet  
 27 and triplet excitons are found to be almost of the same order of magnitude, whether excitons are  
 28 generated in the donor or acceptor in the three types of BHJ OSCs considered here. The higher  
 29 conversion efficiency observed in these BHJ OSCs may therefore be attributed to the added  
 30 contributions of both the excitons generated in the donor as well as in the acceptor.

31  
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## 1 **References**

- 2 1. M. Narayan, J. Singh, *Nanosci. Technol.* **1**, 1-8 (2014)
- 3 2. M. Narayan, J. Singh, *Excitonic and Photonic Processes in Materials* (Springer, New York,
- 4 2015)
- 5 3. L. Huo, T. Liu, X. Sun, Y. Cai, A.J. Heeger, Y. Sun, *Adv. Mater.* **27**, 2938-2944 (2015)
- 6 4. J. Subbiah, B. Purushothaman, M. Chen, T. Qin, M. Gao, D. Vak, F. Scholes, X. Chen, S.E.
- 7 Watkins, G.J. Wilson, *Adv. Mater.* **27**, 702-705 (2015)
- 8 5. M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, *Prog. Photovoltaics* **23**,1-9.
- 9 (2015)
- 10 6. Y.M. Yang, W. Chen, L. Dou, W. Chang, H. Duan, B. Bob, G. Li and Y. Yang. *Nat.*
- 11 *Photonics* **9**, 190-198 (2015)
- 12 7. M. Narayan, J. Singh, *J. Appl. Phys.* **114**, 154515-1 - 15415-7. (2013)
- 13 8. M. Narayan, J. Singh, *Eur. Phys. J. B* **86**, 47-51 (2013)
- 14 9. J. Singh, M. Narayan, D. Ompong, *J. Phys.* **619**, 012030-012036 (2015)
- 15 10. M. Narayan, J. Singh, *Phys. Status Solidi C* **9**, 2386-2389 (2012)
- 16 11. M. Narayan, J. Singh, *Can. J. Phys.* **92**, 853-856 (2013)
- 17 12. C. Deibel, T. Strobel, V. Dyakonov, *Adv. Mater.* **22**, 4097-4111 (2010)
- 18 13. S. Günes, H. Neugebauer, N.S. Sariciftci, *Chem. Rev.* **107**, 1324-1338. (2007)
- 19 14. D. Veldman, S.C. Meskers, R.A. Janssen, *Adv. Funct. Mater.* **19**, 1939-1948. (2009)
- 20 15. T.M. Clarke, J.R. Durrant, *Chem. Rev.* **110**, 6736-6767 (2010)
- 21 16. R. Shivanna, S. Shoaee, S. Dimitrov, S.K. Kandappa, S. Rajaram, J.R. Durrant, K.S. Narayan,
- 22 *Energy Environ. Sci.* **7**, 435-441 (2014)
- 23 17. A. Devižis, J. Jonghe-Risse, R. Hany, F. Nüesch, S. Jenatsch, V. Gulbinas, J. Moser, *J. Am.*
- 24 *Chem. S Soc.* **137**, 8192-8198. (2015)
- 25 18. K. Cnops, B.P. Rand, D. Cheyns, B. Verreert, M.A. Empl, P. Heremans, *Nat. Commun.* **5**, 1-6
- 26 (2014)
- 27 19. W. Zhao, D. Qian, S. Zhang, S. Li, O. Inganäs, F. Gao, J. Hou, *Adv. Mater.* **28**, 4734-4739
- 28 (2016)
- 29 20. C.L. Chochos, N. Tagmatarchis, V.G. Gregoriou, *RSC Adv.* **3**, 7160-7181 (2013)
- 30 21. L.A. Pettersson, L.S. Roman, O. Inganäs, *J. Appl. Phys.* **86**, 487-496 (2010)
- 31 22. Y. Liang, Z. Xu, J. Xia, S. Tsai, Y. Wu, G. Li, Gang, R. Claire, L. Yu, *Adv. Mater.* **22**, E135-
- 32 E138 (2010)
- 33 23. K. Yonezawa, H. Kamioka, T. Yasuda, L. Han, Y. Moritomo, *Jpn. J. Appl. Phys.* **52**, 062405
- 34 (2013)
- 35 24. P.C. Dastoor, C.R. McNeill, H. Frohne, C. Foster, D. Benjamin, F. Christopher, W.J.
- 36 Belcher, W. Campbell, D. Officer, I.M. Blake, P. Thordarson, M. Crossley, S.H. Hush, J.R.
- 37 Reimers, *J. Phys. Chem. C* **111**, 15415-15426 (2007)

- 1 25. N.C. Nicolaidis, B.S. Routley, J.L. Holdsworth, W.J. Belcher, X. Zhou, P.C. Dastoor, *J. Phys.*  
2 *Chem. C* **115**, 7801-7805 (2011)
- 3 26. V. Mihailetschi, L. Koster, J. Hummelen, P. Blom, *Phys. Rev. Lett.* **93**, 216601-1 - 216601-4.  
4 (2004)
- 5 27. M. Narayan, J. Singh, *J. Appl. Phys.* **114**, 073510-1 - 073510-7 (2013)
- 6 28. Z. He, C. Zhong, S. Su, M. Xu, H. Wu, Y. Cao, *Nat. Photonics* **6**, 591-595 (2012)
- 7 29. X. Zhou, X. Fan, X. Sun, Y. Zhang, Z. Zhu, *Nanoscale Res. Lett.* **10**, 1-8 (2015)
- 8 30. G. Zhao, Y. He, Y. Li, *Adv. Mater.* **22**, 4355-4358 (2010)
- 9 31. H. Xu, H. Ohkita, H. Benten, S. Ito, *Jpn. J. Appl. Phys.* **53**, 01AB10 (2013)
- 10 32. P. Vanlaeke, A. Swinnen, I. Haeldermans, G. Vanhoyland, T. Aernouts, D. Cheyns, C.  
11 Deibel, J. D'Haen, P. Heremans, J. Poortmans, *Sol. Energ. Mat. Sol. Cells* **90**, 2150-2158  
12 (2006)
- 13 33. Y. He, H. Chen, J. Hou, Y. Li, *J. Am. Chem. Soc.* **132**, 1377-1382 (2010)
- 14 34. Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nat.*  
15 *Commun.* **5**, 1-8 (2014)
- 16 35. A. Hebard, R. Haddon, R. Fleming, A. Kortan, *Appl. Phys. Lett.* **59**, 2109-2111 (1991)
- 17 36. A.J. Ward, A. Ruseckas, M.M. Kareem, B. Ebenhoch, L.A. Serrano, M. Al-Eid, B.  
18 Fitzpatrick, V.M. Rotello, G. Cooke, D.W. Samuel, *Adv. Mater.* **27**, 2496-2500 (2015)
- 19 37. G.J. Hedley, A.J. Ward, A. Alekseev, C.T. Howells, E.R. Martins, L.A. Serrano, G. Cooke,  
20 A. Ruseckas, I.D. Samuel, *Nat. Commun.* **4**, 1-10 (2013)
- 21 38. Y.-X. Liu, M.A. Summers, S.R. Scully, M.D. McGehee, *J. Appl. Phys.* **99**, 93521-93521  
22 (2006)
- 23 39. Q. An, F. Zhang, J. Zhang, W. Tang, Z. Deng, B. Hu, *Energ. Environ. Sci.* **9**, 281-322 (2016)
- 24 40. V. Gupta, V. Bharti, M. Kumar, S. Chand, A.J. Heeger, *Adv. Mater.* **27**, 4398-4404 (2015)
- 25 41. T. Ameri, T. Heumüller, J. Min, N. Li, G. Matt, U. Scherf, C.J. Brabec, *Energy Environ. Sci.*  
26 **6**, 1796-1801 (2013)
- 27 42. T.V. Pho, F.M. Toma, B.J. T. Villers, S. Wang, N. D. Treat, N. D. Eisenmenger, G. M.  
28 Su, R. C. Coffin, J. D. Douglas, J. M. J. Fréchet, G. C. Bazan, F. Wudl, M. L. Chabinyc, *Adv.*  
29 *Energy Mater.* **4**, 1301007-1 - 1301007-7 (2014)
- 30 43. S. Das, T. Alford, *J. Appl. Phys.* **116**, 044905-5 (2014)
- 31 44. K. Leong, M.E. Foster, B.M. Wong, E.D. Spörcke, D. Van Gough, J.C. Deaton, M.D.  
32 Allendorf, *J. Mater. Chem. A* **2**, 3389-3398 (2014)
- 33 45. S. Cook, A. Furube, R. Katoh, L. Han, *Chem. Phys. Lett.* **478**, 33-36 (2009)
- 34 46. P. Peumans, A. Yakimov, S.R. Forrest, *J. Appl. Phys.* **93**, 3693-3723 (2003)
- 35 47. C.J. Brabec, G. Zerza, G. Cerullo, et al. *Chem. Phys. Lett.* **340**, 232-236 (2001)
- 36 48. D. Ompong, J. Singh, *Chem. Phys. Chem.* **16**, 1281-1285 (2015)
- 37 49. D.F. Kronholm, J.C. Hummelen, *Organic Photovoltaics* (Wiley, Germany, 2008)