**Revealing Optically Induced Dipole-Dipole Interaction Effects on Charge Dissociation
at Donor:Acceptor Interfaces in Organic Solar Cells under Device-Operating Condition**

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1 ***Abstract***

2 Organic materials normally have low dielectric constants and are often formed with high
3 electron-hole binding energy, which are detrimental to the generation of photovoltaic actions
4 in solution-processing thin-film solar cells. Here, we show that optically induced dipole-
5 dipole interaction can largely decrease the electron-hole binding energy at donor:acceptor
6 (D:A) based on the PTB7:PCBM bulk-heterojunctions. Our experimental measurements
7 combine (i) double-beam 325 nm and 532 nm excitations to establish dipole-dipole
8 interaction by selectively exciting the intramolecular charge-transfer donor and optically
9 polarizable acceptor and (ii) magneto-photocurrent to monitor the electron-hole binding
10 energy through charge dissociation at D:A interfaces. We find that the electron-hole binding
11 energy at D:A interfaces can be significantly decreased when the dipole-dipole interaction is
12 optically established in PTB7:PCBM solar cells. Furthermore, the dipole-dipole interaction
13 forms a drifting field to facilitate charge transport, and consequently enhancing the V_{oc} and
14 FF in developing photovoltaic actions in organic solar cells.

15
16 **Keywords: Optically generated dipoles, charge dissociation, organic solar cells,**
17 **magneto-photocurrent.**
18

1 **Introduction**

2 Low bandgap polymers are critical components towards developing high-efficiency
3 organic solar cells with facial materials processing and large-area properties¹⁻⁷. Using
4 coexisted electron-donating and electron-withdrawing units forms an important approach to
5 design advanced photovoltaic polymers with low bandgaps for developing efficient solar
6 cells⁸⁻¹⁰. The typical photovoltaic polymer, namely polythieno[3,4-b]-thiophene-co-
7 benzodithiophene (PTB7), contains both the electron-donating Benzodith-iophene (BDT) and
8 the electron-withdrawing thienothiophene (TT) moieties^{3, 11}. As a consequence, a
9 photoexcitation can generate local electric dipoles between electron-donating and electron-
10 withdrawing moieties, namely intra-chain dipoles, in the donor PTB7 chains¹²⁻¹⁷. The
11 optically generated dipoles have been estimated by calculating the dipole-moment change
12 from ground state to excited state^{13,15-17}. It should be pointed out that the widely used
13 acceptor molecules of fullerene derivatives possess very high polarizabilities in exposure to
14 an electric field^{18,19,20}. With the high polarizabilities a photoexcitation can largely polarize
15 the fullerene molecules, leading to optically polarized acceptor molecules. In this situation
16 the dipole-dipole interaction can be established between donor and acceptor components in
17 bulk-heterojunction solar cells. In principle, the optically induced dipole-dipole interaction
18 can influence the charge dissociation, transport, and collection through drifting field, and
19 consequently changes the J_{sc} , V_{oc} , and FF in bulk-heterojunctions. In this work, we explore
20 the effects of optically induced dipole-dipole interaction on the electron-hole binding energy
21 at D:A interfaces based on the typical PTB7:PCBM solar cells. Our experimental
22 measurements combine two simultaneous procedures: (i) applying the double-beam 532 nm
23 and 325 nm excitations to establish the dipole-dipole interaction between donor and acceptor
24 components and (ii) using magneto-photocurrent to monitor the charge dissociation at the
25 D:A interfaces, in the PTB7:PCBM bulk-heterojunction solar cells. Specifically, adjusting the

double-beam 532 nm and 325 nm excitations can generate three different excited situations: (i) the donor only, (ii) acceptor only, and (iii) both donor and acceptor components to control the dipole-dipole interaction. At the same time, we use magneto-photocurrent with an external electric field to measure the critical bias required to completely dissociate the electron-hole pairs at the D:A interfaces when the dipole-dipole interaction is established between donor and acceptor components. Therefore, combining double-beam excitation with magneto-photocurrent can reveal the dipole-dipole interaction effects on the electron-hole binding energy at the D:A interfaces in bulk-heterojunction solar cells.

The magneto-photocurrent phenomena were originally observed from the photoconduction in pristine organic materials in a low field (< 10 mT) in 1970s.²¹⁻²³ In recent a few years, the magneto-photocurrent studies have been extended to bulk-heterojunctions in organic solar cells²⁴⁻²⁷. In general, the magneto-photocurrent phenomena can be observed when a magnetic field disturbs the populations of different spin states during the generation of photocurrent. Before applying a magnetic field, different spin states can reach certain populations governed by the spin mixing, caused by hyperfine or spin-orbital coupling, and spin-conserving, generated by spin-exchange interaction. In most organic materials where hyperfine interaction is a primary factor responsible for spin mixing normally occurring below 10 mT due to negligible spin-orbital coupling, the spin-exchange interaction can essentially determine whether the populations of different spin states can be disturbed by a magnetic field via introducing in-phase or out-phase spin precessions above the hyperfine regime^{28,29}. In general, the different spin states can exist in both intramolecular and intermolecular states in organic solar cells. The intramolecular states are mainly Frenkel excitons while the intermolecular states present as charge-transfer complexes, similar to polaron pairs. In general, the Frenkel excitons do not exhibit appreciable magneto-photocurrent due to strong spin-exchange interaction which tightly governs the spin

populations^{24,26}. However, the polaron pairs and charge-transfer states can generate appreciable magneto-photocurrent signals at room temperature^{21,24,26}. The experimental studies have shown that a magnetic field can easily disturb the spin-conserving or spin-mixing in polaron pairs and charge-transfer states due to weak spin-exchange interaction^{24,26,27,30}. Specifically, in pristine organic materials the polaron pairs can generate a low-field magneto-photocurrent within hyperfine regime (< 10 mT) due to negligible spin-exchange interaction^{26, 31}. However, in bulk-heterojunctions the low-field magneto-photocurrent from polaron pairs becomes un-detectable²⁴. This indicates that the polaron pairs are completely dissociated by the D:A interfaces. Instead, a new magneto-photocurrent can be observed above the hyperfine regime (> 10 mT) due to appreciable spin-exchange interaction in organic solar cells.^{12,24} These new magneto-photocurrent signals above hyperfine regime have been attributed to the electron-hole pairs at D:A interfaces. In this work, we select the PTB7 and PC₆₀BM as donor and acceptor to fabricate the bulk-heterojunction PTB7:PC₆₀BM solar cells. In particular, the separated absorption spectra between PTB7 and PC₆₀BM allows that the donor and acceptor components can be separately excited by using double-beam 532 nm and 325 nm excitations in the PTB7:PC₆₀BM solar cells. We notice that the PTB7:PC₇₀BM system exhibits a higher photovoltaic action with the PCE of around 9.2 % as compared to the PTB7:PC₆₀BM system with the PCE of 7.4%. However, the PTB7:PC₇₀BM system possesses an overlap between PTB7 and PC₇₀BM optical absorption spectra (as shown in Figure 5 (b)), leading to an experimental difficulty to reveal the electrical interaction between donor and acceptor components by using double-beam excitations. Based on the PTB7:PC₆₀BM system with separated optical absorption spectra, combining the magneto-photocurrent with an external bias provides an experimental method to explore the electron-hole binding energy at the D:A interfaces in the PTB7:PC₆₀BM solar cells when the electrical interaction is optically changed by separately

exciting the donor only, acceptor only, and both donor and acceptor components. Essentially, the electron-hole binding energy at the D:A interfaces can be evaluated by the critical bias required to completely quench the magneto-photocurrent generated by electron-hole pairs in the PTB7:PC₆₀BM solar cells.

Experimental Section

The experimental studies were performed based on the typical solar cell: PTB7:PCBM bulk-heterojunctions where the dipole-dipole interaction can be optically established between the donor-PTB7 and the acceptor-PCBM under photoexcitation. The PTB7 was synthesized according to a previously reported method³². The fullerene acceptor materials, PC₆₀BM and PC₇₀BM, together with electrolyte PFN were purchased from 1-material Chemscitech and used to fabricate the ITO/PFN/PTB7:PCBM/MoO₃/Ag devices. The PFN was spin-coated on pre-cleaned ITO glass substrates from a solution of 2mg/ml in methanol with a small volume of acetic acid (2μl/ml). Here, the major isomers are 3'H-Cyclopropa[8,25][5,6]fullerene-C60-D5h(6)-3'-butanoic acid and 3'-phenyl-, methyl ester in the PC₆₀BM and 3'H-Cyclopropa[8,25][5,6]fullerene-C70-D5h(6)-3'-butanoic acid and 3'-phenyl-, methyl ester in the PC₇₀BM. The PTB7:PC₆₀BM and PTB7:PC₇₀BM composites were prepared with the weight ratios of 1:1 and 1:1.5, respectively, in chlorobenzene/1,8-diiodooctane mixture solvent (97ml:3ml). The solution concentrations of PTB7:PC₆₀BM and PTB7:PC₇₀BM composites were set at 20mg/ml and 25mg/mL. The PTB7:PCBM films were spin cast with the thickness of 100nm on the charge-transporting PFN layers. The charge-transporting MoO₃ layers and Ag electrodes were thermally deposited under the vacuum of 7×10^{-7} torr with film thicknesses of 10nm and 40nm, respectively. The effective device operating area is 6 mm² under simulated sunlight illumination and 3.14 mm² under CW laser light illumination. The current-voltage (*I-V*) characteristics were measured by using Keithley 2400 source meter

under simulated sunlight (Thermal Oriel 96000 300 W from Newport) and continuous wave (CW) laser excitations (532nm and 325nm). The capacitance-frequency measurement were performed under different frequencies by using a dielectric spectrometer (Agilent E4980A LCR). The magneto-photocurrent signals were recorded by measuring the short-circuit current as a function of magnetic field. The optical absorption spectra were recorded from solid films with the thickness of 100 nm for all blends (PTB7:PC₆₀BM with 20mg/mL and PTB7:PC₇₀BM with 25mg/mL), 63 nm for PTB7, and 54 nm for PCBM (PC₆₀BM and PC₇₀BM) on quartz substrates by using UV/VIS spectrometer (Lambda 35, PerkinElmer Instruments) under transmission mode. The control-experiments indicate that the observed magneto-photocurrent is originated from the electron-hole pairs at the D:A interfaces in the PTB7:PC₆₀BM solar cells by comparing the pristine donor-PTB7 and the PTB7:PC₆₀BM bulk-heterojunction samples. The magneto-photocurrents were recorded by measuring the photocurrent (J_{sc}) as a function of magnetic field at room temperature. The magneto-photocurrent amplitude is defined as $\frac{I_B - I_0}{I_0}$, where the I_B and I_0 are the photocurrents with and without magnetic field at short-circuit condition. By combining the magneto-photocurrent measurements with a reversed external bias, the electron-hole binding energy at D:A interfaces was evaluated by the critical bias required to completely quench the magneto-photocurrent signal at different excitation intensities. The dipole-dipole interaction between donor and acceptor components were optically tuned by separately exciting (i) the donor-PTB7 only, (ii) the acceptor-PC₆₀BM only, and (iii) both the donor-PTB7 and acceptor-PC₆₀BM, in the PTB7:PC₆₀BM solar cells with using the double-beam excitation of 532 nm and 325 nm. All measurements were performed under nitrogen gas atmosphere at room temperature.

Results and discussion

Figure 1(a) shows the magneto-photocurrent signals measured above the hyperfine regime from the ITO/PFN/PTB7:PC₆₀BM/MoO₃/Ag device under two different excitations by using (i) 532 nm beam of exciting the donor-PTB7 and (ii) simulated sunlight of exciting both donor and acceptor components. When the 532 nm beam of 100 mW/cm² is used to only excite the donor-PTB7, a magneto-photocurrent signal can be clearly observed in the PTB7:PC₆₀BM solar cell. The observed magneto-photocurrent indicates that the electron-hole pairs are formed as charge-transfer states at the D:A interfaces during the generation of photocurrent. However, when the simulated sunlight at one-sun condition (100 mW/cm² white light) is used to excite both donor and acceptor, the magneto-photocurrent becomes non-detectable in the PTB7:PC₆₀BM solar cells. We note that the 532 nm laser beam of 100 mW/cm² is stronger than the simulated sun light at one-sun condition by a factor of 2.6. However, further increasing the simulated sun light to three-sun condition (300 mW/cm²) does not generate any detectable magneto-photocurrent signal. When the 532 nm laser beam intensity decreases to 24 mW/cm² to only excite the donor-PTB7, slightly lower than sun light (one-sun condition), a magneto-photocurrent signal can be still observed (Figure 1(a)). Therefore, our experimental observation indicates that exciting both donor and acceptor by using simulated sunlight disables the formation of electron-hole pairs at D:A interfaces in the PTB7:PC₆₀BM solar cells. This phenomenon opens an important question: how can the simulated sunlight completely dissociate the electron-hole pairs at the D:A interfaces? We should note from absorption spectra that the donor-PTB7 and acceptor-PCBM do not mutually interact, functioning as mechanic mixture in dark condition before applying sunlight illumination, based on the pure additivity of two individual absorption spectra (as shown in Figure S1 in supporting material). Under photoexcitation, we propose that the simulated sunlight generates an electrical interaction between donor and acceptor components by exciting both the donor-PTB7 and acceptor-PC₆₀BM, and consequently dissociates the

electron-hole pairs at the D:A interfaces. Essentially, exciting both donor and acceptor generates an electrical dipole in the PTB7 through intramolecular charge transfer and the electrical polarization in the PC₆₀BM through excited states, leading to a dipole-dipole interaction between the PTB7 and the PC₆₀BM in the PTB7:PC₆₀BM solar cells (Figure 1 (b)). Specifically, exciting the donor-PTB7 generates both excitons and electrical dipoles. Exciting the acceptor-PC₆₀BM can lead to largely polarized acceptor molecules due to high polarizabilities. As a consequence, a dipole-dipole interaction can occur between the PTB7 and PC₆₀BM components in the bulk-heterojunction (PTB7:PC₆₀BM) system. The photoluminescence quenching shows that the photoexcited excitons can predominately dissociate into free carriers in donor and acceptor components^{33,34}. But, the free carriers can partially recombine into electron-hole pairs, namely charge-transfer states, at the D:A interfaces³⁵⁻³⁷. Obviously, the electron-hole pairs are exposed to the dipole-dipole interaction formed between the donor and acceptor components during the generation of photovoltaic actions (Figure 1 (c)). Here, we can see that the dipole-dipole interaction between donor and acceptor components provides a primary driving force to dissociate the electron-hole pairs at the D:A interfaces in bulk-heterojunction solar cells.

We should note that the optically generated dipoles in the donor-PTB7 are the necessary parameter in the dipole-dipole interaction between the PTB7 and PC₆₀BM components. To confirm the optically generated dipoles in PTB7, we investigate the capacitance-frequency (*C-f*) characteristics upon simulated sunlight illumination. It is known that the low and high-frequency *C-f* characteristics are generated by electrode interfaces and bulk in the electrode/semiconductor/electrode devices³⁸. Essentially, the high-frequency *C-f* characteristics can reflect the bulk polarization upon applying light illumination. Figure 2 shows the high-frequency *C-f* characteristics based on single layer PTB7 and P3HT devices with the architecture of Ag/polymer/Ag. We can see that increasing the light intensity from

0.3 sun to 1 sun condition can cause a much larger change (19%) in the Ag/PTB7/Ag device as compared to a much smaller change (7.8%) in the Ag/P3HT/Ag device at high frequency regime ($> 1.0 \times 10^6$ Hz), as shown in Figure 2 (a) and (b). This indicates that the PTB7 exhibits stronger bulk polarization than the P3HT under optical excitation. The PTB7 chain possesses an intramolecular donor-acceptor structure between BDT and TT units, forming a mechanism to generate an electrical dipole upon optical excitation. However, the P3HT chain lacks the mechanism to generate an electrical dipole due to the absence of intramolecular donor-acceptor structure. Therefore, the observed stronger bulk polarization provides an evidence to confirm the formation of optically generated dipoles in the PTB7 upon light illumination. Now we consider whether optically generated dipoles can be partially aligned in the PTB7 by built-in field. We know that the PTB7 is formed amorphous structure in a spin-cast film. In principle, an amorphous structure can lead to random dipoles, causing negligible net dipole moment in the PTB7 film. In this situation the electrical interaction between the donor-PTB7 and the acceptor-PC₆₀BM would be difficult to influence the charge dissociation at the D:A interfaces in the PTB7:PC₆₀BM solar cells. However, the optically generated dipoles can be partially aligned through dipole migration within an amorphous PTB7 chain under the influence of built-in field in electrode/polymer/electrode devices. We can see in Figure 2 (c) and (d) that applying a reverse bias of -0.9 V can largely increase the high-frequency $C-f$ signal by 11.9% in the Ag/PTB7/Ag device but only 3.3% in the Ag/P3HT/Ag device. This result shows that an external field can interact with the optically generated dipoles in the PTB7 and largely increases the bulk polarization. This provides an experimental information to support that optically generated dipoles can be partially aligned, leading to a net dipole moment in the amorphous PTB7 for generating an electrical interaction between the PTB7 and PC₆₀BM components in the PTB7:PC₆₀BM solar cells.

To understand the electrical interaction effects on charge dissociation, we need to monitor the electron-hole pairs at D:A interfaces. It is known that the photoexcited excitons can be significantly dissociated in the bulk-heterojunction PTB7:PC₆₀BM solar cells^{39,40}. However, the magneto-photocurrent signal (Figure 1 (a)) clearly indicates that the photogenerated charge carriers can inevitably form electron-hole pairs at the D:A interfaces^{12,24}. Here, magneto-photocurrent provides an experimental tool to monitor the electron-hole pairs at D:A interfaces in organic solar cells. Essentially, the electron-hole pairs are formed with both spin-antiparallel and spin-parallel states with the 1:3 ratio through randomly pairing process. A magnetic field can change the populations of spin-antiparallel and spin-parallel pairs by influencing spin precessions in electron-hole pairs, and consequently modifies the photocurrent due to different dissociation rates, generating a magneto-photocurrent signal. Therefore, magneto-photocurrent can be used as an *in-situ* method to monitor the electron-hole pairs at D:A interfaces in organic solar cells under device-operating condition. Furthermore, we should note that applying an external bias can dissociate the electron-hole pairs formed at the D:A interfaces, decreasing magneto-photocurrent signal. The electron-hole pairs can be completely dissociated when an external bias increases to a critical value, leading to un-detectable magneto-photocurrent. Essentially, this critical bias can give an estimate on the electron-hole binding energy. Therefore, combining an external critical bias and magneto-photocurrent can provide an experimental method, namely bias-dependent magneto-photocurrent, to estimate the electron-hole binding energy at the D:A interfaces in organic solar cells.

Now we investigate the effects of dipole-dipole interaction on electron-hole binding energy at the D:A interfaces with bias-dependent magneto-photocurrent by using the double-beam 532 nm and 325 nm excitations to separately excite the donor and acceptor components in the PTB7:PC₆₀BM solar cells. At the constant intensity of 532 nm of exciting donor-PTB7,

adding the second excitation of 325 nm to excite the acceptor-PC₆₀BM component can gradually quench the magneto-photocurrent signal (Figure 3 (a)). This result provides the first experimental evidence to support our hypothesis that exciting both donor and acceptor can establish the dipole-dipole interaction between donor and acceptor components and consequently decreases the electron-hole pairs at the D:A interfaces. With the reduction of magneto-photocurrent magnitude, we can make an argument that optically exciting the PC₆₀BM mainly induce the electrical polarization in the acceptor and consequently enhances the dipole-dipole interaction between the donor and acceptor components with the consequence of dissociating the electron-hole pairs at the D:A interfaces. Furthermore, we can see in Figure 3 (b) that, at the constant intensity of 325 nm beam of exciting the acceptor-PC₆₀BM, increasing the 532 nm beam intensity of exciting the donor-PTB7 increases the magneto-photocurrent amplitude (Figure 3 (b)). The magneto-photocurrent amplitude increases from 0.94 % to 1.73 % and 2.17 % when the 532 nm excitation is increased from 60 mW/cm² to 82 mW/cm² and 100 mW/cm² at the constant intensity of 325 nm beam intensity of 14 mW/cm². This increasement of magneto-photocurrent indicates that increasing the 532 nm beam intensity of exciting the donor-PTB7 component can essentially increase the electron-hole pairs at the D:A interfaces, in addition to introducing the dipoles in the donor component. Nevertheless, simultaneously exciting the donor-PTB7 and the acceptor-PC₆₀BM can establish dipole-dipole interaction between donor and acceptor components in the bulk-heterojunction PTB7:PC₆₀BM solar cells.

Now we characterize the electron-hole binding energy at the D:A interfaces as a function of dipole-dipole interaction in the PTB7:PC₆₀BM solar cells. Here we use the critical bias required to completely quench the magneto-photocurrent signal to estimate the electron-hole binding energy at the D:A interfaces. The critical bias was measured in two different situations: (i) changing the 532 nm beam intensity of exciting the donor at the constant

1 intensity of 325 nm of exciting the acceptor and (ii) changing the 325 nm beam intensity of
2 exciting the acceptor at the constant intensity of 532 nm of exciting the donor. Here, we can
3 see a surprising phenomenon: increasing the 325 nm beam intensity of exciting the acceptor-
4 PC₆₀BM can largely decrease the critical bias required to remove magneto-photocurrent
5 signal (Figure 3 (a)). Without the 325 nm beam of exciting the acceptor- PC₆₀BM, the critical
6 bias becomes 895 mV. When the 325 nm beam intensity is increased from 5 mW/cm² to 10
7 mW/cm² and 14 mW/cm², the critical bias largely decreases from 775 mV to 550 mV and a
8 negligible value. This means that establishing the dipole-dipole interaction by exciting both
9 the donor-PTB7 and acceptor-PC₆₀BM can largely decrease the electron-hole pairs at the D:A
10 interfaces, leading to an enhanced charge dissociation in the PTB7:PC₆₀BM solar cells.
11 Furthermore, at the constant intensity of 325 nm of exciting the acceptor-PC₆₀BM, increasing
12 the 532 nm beam intensity of exciting the donor-PTB7 beam decreases the critical bias,
13 required to completely quench the magneto-photocurrent signal, from 350 mV to 215 mV and
14 155 mV while the magneto-photocurrent amplitude is increased from 0.94 % to 1.73 % and
15 2.17 %. This leads to an interesting situation: the charge dissociation at the D:A interfaces
16 becomes easier as the electron-hole pairs are increased. Normally, increasing the electron-
17 hole pairs at the D:A interfaces would require a higher critical bias to complete the charge
18 dissociation. Obviously, this interesting situation reflects the dipole-dipole interaction effects.
19 Specifically, increasing the 532 nm beam intensity of exciting the donor can simultaneously
20 increase both the intra-chain dipoles in the PTB7 and the electron-hole pairs at the
21 PTB7:PC₆₀BM interfaces. The intra-chain dipoles in the PTB7 can form the dipole-dipole
22 interaction with the excited PC₆₀BM component in the PTB7:PC₆₀BM bulk-heterojunctions.
23 The inversion relationship between the critical bias and density of electron-hole pairs
24 indicates that the dipole-dipole interaction can indeed decrease the electron-hole binding
25 energy at the D:A interfaces. Nevertheless, by separately exciting the donor and acceptor, our

magneto-photocurrent studies can confirm that the dipole-dipole interaction between the donor and acceptor components can decrease the electron-hole binding energy at the D:A interfaces, enhancing charge dissociation in the PTB7:PCBM bulk-heterojunctions.

Here we use the P3HT:PC₆₀BM bulk-heterojunctions, where the dipole-dipole interaction is absent, to further understand the optically induced dipole-dipole interaction. It should be pointed out that the P3HT does not have co-existed electron-donating and electron-withdrawing units. Optically exciting the P3HT can only generate photoexcited excitons without generating intra-chain dipoles in the P3HT chains. As a consequence, the P3HT:PC₆₀BM bulk-heterojunctions do not exhibit dipole-dipole interaction between the donor and acceptor components when both the donor and acceptor are excited under simulated sunlight. It is interesting to see in Figure 4 that the simulated sunlight generates the magneto-photocurrent signal above 200 mT in the P3HT:PC₆₀BM solar cell. This high-field magneto-photocurrent signal results from the electron-hole pairs at the D:A interfaces^{24,26,41}. Obviously, the electron-hole pairs are still existed in the P3HT:PC₆₀BM bulk-heterojunctions, opposite to the PTB7:PC₆₀BM bulk-heterojunctions where the electron-hole pairs become non-detectable, under simulated sunlight. Contrarily to the PTB7:PC₆₀BM bulk-heterojunctions, in the P3HT:PC₆₀BM bulk-heterojunctions both the magneto-photocurrent amplitude and the critical bias increases upon increasing photoexcitation. The critical bias is increased from 0.37 V to 0.5 V while the magneto-photocurrent magnitude increases from 0.21 % to 0.34 % (the value at 800 mT) when the sunlight intensity of exciting both the donor-P3HT and acceptor-PC₆₀BM is changed from 50 mW/cm² to 100 mW/cm². This result shows that increasing the electron-hole pairs requires a higher critical bias to complete the charge dissociation upon increasing the beam intensity of 532 nm exciting the donor-P3HT in the P3HT:PC₆₀BM bulk-heterojunctions. On contrast, in the PTB7:PC₆₀BM solar cells increasing the electron-hole pairs requires a lower critical bias to complete the charge

dissociation with increasing the beam intensity of 532 nm of exciting the donor-PTB7. Clearly, this profound difference in the critical bias dependence between the P3HT and PTB7 based solar cells provides further evidence that the dipole-dipole interaction between the donor and acceptor components play an important role to dissociate the electron-hole pairs at the D:A interfaces towards the generation of photovoltaic actions in organic solar cells.

We should note that the electrical potential energies from the critical biases are much lower than the electron-hole binding energies in the PTB7:PC₆₀BM and P3HT:PC₆₀BM systems. It should be pointed out that organic solar cells can exist charged defects and trapped carriers in both bulk and electrode interfaces, generating local polarizations under photoexcitation⁴²⁻⁴⁶. An applied bias can interact with these local polarizations to dissociate the electron-hole pairs. As a consequence, even an external bias does not provide enough potential energies to overcome the electron-hole binding energy, it can still increase the charge dissociation through local polarizations in organic solar cells⁴⁷⁻⁵⁰. Nevertheless, the critical bias required to completely quench magneto-photocurrent can be used to reflect the electron-hole binding energy at the D:A interfaces. It should be also noted that the PTB7:PC₆₀BM bulk-heterojunctions form an amorphous morphology with three structures: PTB7 phase, PC₆₀BM phase, and mixed PTB7:PC₆₀BM phase^{51,52}. The D:A interfaces can exist both between the PTB7 and PC₆₀BM phases and within the mixed PTB7:PC₆₀BM phase. We should also note that within amorphous structures the optically generated dipole-dipole interaction between donor and acceptor components can be isotropically formed within the active PTB7:PC₆₀BM film. However, our studies indicate that the dipole-dipole interaction still exists in the amorphous PTB7:PC₆₀BM bulk-heterojunctions. This means that the built-in field under device-operating condition can induce a certain orientation on the dipole-dipole interaction in amorphous bulk-heterojunctions. As a result, the dipole-dipole

interaction can influence the electron-hole binding energy at the D:A interfaces in organic solar cells.

Here, we verify the effects of optically generated dipole-dipole interaction on photovoltaic actions. Specifically, the double-beam excitations are adjusted to a similar photocurrent generated by simulated sunlight. In this situation, the double-beam and simulated sunlight have the same nominal intensity for generating a common photocurrent. We can see in Figure 3 that the double-beam 325 nm and 532 nm excitations at 14 mW/cm² and 24 mW/cm² lead to un-detectable magneto-photocurrent in the PTB7:PC₆₀BM solar cells. This means that, by the 14 mW/cm² from 325 nm beam and 24 mW/cm² from 532 nm beam, the optically dipole-dipole interaction can sufficiently dissociate the electron-hole pairs at the D:A interfaces. More importantly, combining the 14 mW/cm² from 325 nm beam and 24 mW/cm² from 532 nm beam produces a similar photocurrent as compared to the simulated sunlight in the PTB7:PC₆₀BM system. In this situation, the double-beam and simulated sunlight have the same nominal intensity. Under the same nominal intensity, we can see that the simulated sunlight generates larger *FF* and *V_{oc}* relative to the double-beam 532 nm and 325 nm excitations (Figure 5 (a)). In the PTB7:PC₆₀BM system the *FF* and *V_{oc}* are determined to be 59% and 0.72V under simulated sunlight operation. However, the *FF* and *V_{oc}* are slightly decreased to 51% and 0.70V under the double-beam 532 nm and 325 nm excitations with the same minimal intensity. We know that simulated sunlight operation can lead to more dipole-dipole interaction due to broad-range absorption as compared to the double-beam 532nm and 325nm excitations. The deference in *FF* and *V_{oc}* between simulated sunlight and double-beam operations reflects that the optically generated dipole-dipole interaction can essentially enhance the charge transport and built-in field during the *FF* and *V_{oc}* developments. Furthermore, we test the simulated sunlight and double-beam operations with the same nominal intensity based on the PTB7:PC₇₀BM system. It is known that the

PTB7:PC₇₀BM device can generate higher photovoltaic efficiency as compared to the PTB7:PC₆₀BM device (9.2 % versus 7.4 %). However, in the PTB7:PC₇₀BM system the donor and acceptor have a certain overlap in optical absorption. This spectral overlap causes a difficulty to separately excite the donor and acceptor by using double-beam 532 nm and 325 nm excitations to reveal the effects of optically generated dipole-dipole interaction on photovoltaic actions. But, we can see in the PTB7:PC₇₀BM system that the simulated sunlight operation leads to much higher FF and V_{oc} as compared to the double-beam (325nm-14mW/cm² and 532nm-33mW/cm²) operation (65% and 0.72V versus 52% and 0.70V), as shown in Figure 5(a). Nevertheless, this result from the PTB7:PC₇₀BM system further confirms the effects of dipole-dipole interaction on photovoltaic actions. Clearly, our I - V characterization indicates that optically generated dipole-dipole interaction can strengthen charge dissociation, charge transport, and built-in field during photovoltaic development in organic solar cells. Therefore, optically generated dipole-dipole interaction can function as an effective method to enhance photovoltaic actions in low-dielectric organic materials.

We should note that the dipole-dipole interaction at donor:acceptor interface is essentially determined by three factors: (i) the optically generated electrical dipoles in donor component, (ii) the electrical polarizability in acceptor component, and (iii) the dielectric constant under photoexcitation. Firstly, the optically generated dipoles are generated by intrachain charge transfer between the electron-donating (Benzodith-iophene (BDT) and electron-accepting (thienothiophene (TT) units in the PTB7. The intrachain charge transfer is thus controlled by the difference in electron negativity between electron-donating and electron-accepting units in the donor component. Secondly, the electrical polarizability in the acceptor component occurs by polarizing process of delocalized semiconducting π electrons. Thirdly, the dielectric constant in organic materials can be increased under photoexcitation. This can also affect the dipole-dipole interaction at donor:acceptor interface through

Coulomb screening effect⁵³. Therefore, considering these three factors becomes a practical approach to control the dipole-dipole interaction at donor:acceptor interface towards the enhancement of photovoltaic actions in bulk-heterojunction solar cells.

Conclusion

In summary, we use double-beam 532 nm and 325 nm excitations to separately excite the donor-PTB7 and acceptor-PC₆₀BM components to establish the dipole-dipole interaction in the PTB7:PCBM solar cells. The dipole-dipole interaction essentially originates from the Coulomb interaction between optically generated PTB7-dipoles and optically polarized PC₆₀BM under sunlight excitation. At the same time, we use the critical bias required to completely quench the magneto-photocurrent to characterize the electron-hole binding energy at the D:A interfaces when the dipole-dipole interaction is optically tuned by separately controlling the 532 nm and 325 nm excitations. We observe a surprising phenomenon: increasing the density of electron-hole pairs at the D:A interfaces decreases the critical bias to completely dissociate the electron-hole pairs in the PTB7:PC₆₀BM solar cells when both the donor-PTB7 and acceptor-PC₆₀BM are excited to establish dipole-dipole interaction between donor and acceptor components. This indicates that optically generated dipole-dipole interaction can facilitate the charge dissociation at the D:A interfaces in the PTB7:PC₆₀BM solar cells. Contrarily, when the optically generated dipoles are absent, increasing the density of electron-hole pairs at the D:A interfaces causes an increase on the critical bias to completely dissociate the electron-hole pairs in the P3HT:PC₆₀BM solar cells. By comparing these two opposite phenomena, we can see that optically generated dipole-dipole interaction plays an important role to dissociate the electron-hole pairs at the D:A interfaces in organic solar cells. Simultaneously, we can see that the dipole-dipole interaction can increase the V_{oc} and FF by comparing the I - V characteristics measured by double-beam excitations and

1 simulated sunlight at the same nominal intensity. Clearly, our experimental studies reveal that
2 optically generated dipole-dipole interaction is an important issue to control the photovoltaic
3 actions in organic bulk-heterojunction solar cells.

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Figure Captions

Figure 1. (a) Magneto-photocurrent in ITO/PFN/PTB7:PC₆₀BM/MoO₃/Ag device by separately using by 532nm CW laser light (100mW/cm² and 24mW/cm²) and simulated sun light (1 sun, 2 sun, and 3 sun). (b) The diagram to show intra-chain dipoles (blue arrow) in donor-PTB7 and optically induced polarization (red arrow) in acceptor-PC₆₀BM. (c) The diagram to show optically generated dipole-dipole interaction formed between donor and acceptor components to dissociate electron-hole pairs at D:A interfaces in PTB7:PCBM bulk-heterojunctions. Two arrows represent dipole and polarization in donor and acceptor with dipole-dipole interaction.

Figure 2. (a) Capacitance-frequency characteristics under various reverse biases at one sun condition for PTB7 single layer device. (b) Capacitance-frequency characteristics under various reverse biases at one sun condition for P3HT single layer device. (c) Capacitance-frequency characteristics under various simulated sunlight intensities at -0.9V reverse bias for PTB7 single layer device. (d) Capacitance-frequency characteristics under various simulated sunlight intensities at -0.9V reverse bias for P3HT single layer device.

Figure 3. Magneto-photocurrents measured by separately exciting donor-PTB7 and acceptor-PC₆₀BM. (a) Changing 325 nm intensity of exciting acceptor-PC₆₀BM at constant 532 nm intensity (24mW/cm²) of exciting donor-PTB7. (b) Changing 532 nm intensity of exciting donor-PTB7 at constant 325 nm intensity (14mW/cm²) of exciting acceptor-PC₆₀BM. The critical bias (V_c) is given by the reverse bias required to completely quench magneto-photocurrent signal at each condition.

Figure 4. Magneto-photocurrents measured at different excitation intensities under simulated sunlight in ITO/PEDOT:PSS/P3HT:PC₆₀BM/Ca/Al device. The critical bias (V_c) is determined by the reverse bias required to completely quench magneto-photocurrent signal at each excitation intensity.

Figure 5. (a) The I - V characteristics measured by double-beam 325 nm (14mW/cm²) and 532nm (24mW/cm²) and simulated sunlight excitation for ITO/PFN/PTB7:PC₆₀BM/MoO₃/Ag and ITO/PFN/PTB7:PC₇₀BM/MoO₃/Ag devices. (b) Absorption spectra for donor-PTB7, acceptor-PC₆₀BM, and acceptor-PC₇₀BM.

Figure 1. (a) Magneto-photocurrent in ITO/PFN/PTB7:PC₆₀BM/MoO₃/Ag device by separately using by 532nm CW laser light (100mW/cm² and 24mW/cm²) and simulated sun light (1 sun, 2 sun, and 3 sun). (b) The diagram to show intra-chain dipoles (blue arrow) in donor-PTB7 and optically induced polarization (red arrow) in acceptor-PC₆₀BM. (c) The diagram to show optically generated dipole-dipole interaction formed between donor and acceptor components to dissociate electron-hole pairs at D:A interfaces in PTB7:PCBM bulk-heterojunctions. Two arrows represent dipole and polarization in donor and acceptor with dipole-dipole interaction.

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Figure 2. (a) Capacitance-frequency characteristics under various reverse biases at one sun condition for PTB7 single layer device. (b) Capacitance-frequency characteristics under various reverse biases at one sun condition for P3HT single layer device. (c) Capacitance-frequency characteristics under various simulated sunlight intensities at -0.9V reverse bias for PTB7 single layer device. (d) Capacitance-frequency characteristics under various simulated sunlight intensities at -0.9V reverse bias for P3HT single layer device.

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1 References

- 1 Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, *Adv. Mater.* 22 (2010) E135-138.
- 2 S. J. Lou, J. M. Szarko, T. Xu, L. Yu, T. J. Marks, L. X. Chen, *J. Am. Chem. Soc.* 133 (2011) 20661-20663.
- 3 G. Li, V. Shrotriya, Y. Yao, J. Huang, Y. Yang, *J. Mater. Chem.* 17 (2007) 3126-3140.
- 4 Z. He, C. Zhong, S. Su, M. Xu, H. Wu, Y. Cao, *Nat Photon.* 6 (2012) 591-595.
- 5 L. Dou, J. You, J. Yang, C.-C. Chen, Y. He, S. Murase, T. Moriarty, K. Emery, G. Li, Y. Yang, *Nat Photon.* 6 (2012) 180-185.
- 6 Y. Zhong, M. T. Trinh, R. Chen, W. Wang, P. P. Khlyabich, B. Kumar, Q. Xu, C.-Y. Nam, M. Y. Sfeir, C. Black, *J. Am. Chem. Soc.* 136 (2014) 15215-15221.
- 7 J.-M. Jiang, M.-C. Yuan, K. Dinakaran, A. Hariharan, K.-H. Wei, *J. Mater. Chem. A* 1 (2013) 4415-4422.
- 8 S. C. Price, A. C. Stuart, L. Yang, H. Zhou, W. You, *J. Am. Chem. Soc.* 133 (2011) 4625-4631.
- 9 X. Zhang, T. T. Steckler, R. R. Dasari, S. Ohira, W. J. Potscavage, S. P. Tiwari, S. Coppee, S. Ellinger, S. Barlow, J.-L. Bredas, B. Kippelen, J. R. Reynolds, S. R. Marder, *J. Mater. Chem.* 20 (2010) 123-134.
- 10 M. Wang, X. Hu, P. Liu, W. Li, X. Gong, F. Huang, Y. Cao, *J. Am. Chem. Soc.* 133 (2011) 9638-9641.
- 11 H. Zhou, L. Yang, W. You, *Macromolecules* 45 (2012) 607-632.
- 12 H. Zang, Y. Liang, L. Yu, B. Hu, *Adv. Energy Mater.* 1 (2011) 923-929.
- 13 B. Carsten, J. M. Szarko, H. J. Son, W. Wang, L. Lu, F. He, B. S. Rolczynski, S. J. Lou, L. X. Chen, L. Yu, *J. Am. Chem. Soc.* 133 (2011) 20468-20475.
- 14 T. Xu, L. Lu, T. Zheng, J. M. Szarko, A. Schneider, L. X. Chen and L. Yu, *Adv. Funct. Mater.* 24 (2014) 3432-3437.
- 15 B. S. Rolczynski, J. M. Szarko, H. J. Son, L. Yu, L. X. Chen, *J. Phys. Chem. Lett.* 5 (2014) 1856-1863.
- 16 B. Carsten, J. M. Szarko, L. Lu, H. J. Son, F. He, Y. Y. Botros, L. X. Chen, L. Yu, *Macromolecules* 45 (2012) 6390-6395.
- 17 B. S. Rolczynski, J. M. Szarko, H. J. Son, Y. Liang, L. Yu, L. X. Chen, *J. Am. Chem. Soc.* 134 (2012) 4142-4152.
- 18 D. S. Sabirov, *RSC Adv.* 4 (2014) 44996-45028.

-
- 19 K. Akhtari, K. Hassanzadeh, B. Fakhraei, H. Hassanzadeh, G. Akhtari, S. A. Zarei, *Computational and Theoretical Chemistry* 1038 (2014) 1-5.
 - 20 K. Akaike, K. Kanai, H. Yoshida, J. y. Tsutsumi, T. Nishi, N. Sato, Y. Ouchi, K. Seki, J. *Appl. Phys.* 104 (2008) 023710.
 - 21 B. Brocklehurst, R. Dixon, E. Gardy, V. Lopata, M. Quinn, A. Singh, F. Sargent, *Chem. Phys. Lett.* 28 (1974) 361-363.
 - 22 K. Schulten, H. Staerk, A. Weller, H.-J. Werner, B. Nickel, *Zeitschrift für Physikalische Chemie* 101 (1976) 371-390.
 - 23 K. Okamoto, N. Oda, A. Itaya, S. Kusabayashi, *Chem. Phys. Lett.* 35 (1975) 483-486.
 - 24 Z. H. Xu, B. Hu, *Adv. Funct. Mater.* 18 (2008) 2611-2617.
 - 25 Y. Zhang, T. P. Basel, B. R. Gautam, X. Yang, D. J. Mascaró, F. Liu, Z. V. Vardeny, *Nat. commun.* 3 (2012) 1043.
 - 26 B. Hu, L. Yan, M. Shao, *Adv. Mater.* 21 (2009) 1500-1516.
 - 27 F. Wang, H. Bässler, Z. V. Vardeny, *Phys. Rev. Lett.* 101 (2008) 236805.
 - 28 Bayliss, N. C. Greenham, R. H. Friend, H. Bouchiat, A. D. Chepelianskii, *Nat. Commun.* 6 (2015) 8534.
 - 29 L. He, M. Li, A. Urbas, B. Hu, *Phys. Rev. B* 89 (2014) 155304.
 - 30 A. Schellekens, W. Wagemans, S. Kersten, P. Bobbert, B. Koopmans, *Phys. Rev. B* 84 (2011) 075204.
 - 31 W. Wagemans, W. Engelen, F. Bloom, B. Koopmans, *Synt. Met.* 160 (2010) 266-270.
 - 32 Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray, L. Yu, *J. Am. Chem. Soc.* 131 (2009) 7792.
 - 33 Y. Kim, S. A. Choulis, J. Nelson, D. D. Bradley, S. Cook, J. R. Durrant, *J. Mater. Sci.* 40 (2005) 1371-1376.
 - 34 Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. Bradley, M. Giles, I. McCulloch, C.-S. Ha, *Nat. Mater.* 5 (2006) 197-203.
 - 35 S. De, T. Pascher, M. Maiti, K. G. Jespersen, T. Kesti, F. Zhang, O. Inganäs, A. Yartsev, V. Sundström, *J. Am. Chem. Soc.* 129 (2007) 8466-8472.
 - 36 R. C. MacKenzie, T. Kirchartz, G. F. Dibb, J. Nelson, *J. Phys. Chem. C* 115 (2011) 9806-9813.
 - 37 T. M. Clarke, A. M. Ballantyne, J. Nelson, D. D. Bradley, J. R. Durrant, *Adv. Funct. Mater.* 18 (2008) 4029-4035.

-
- 38 C. Zhao, B. Chen, X. Qiao, L. Luan, K. Lu, B. Hu, *Adv. Energy Mater.* 5 (2015) doi:10.1002/aenm.20157007.
- 39 S. Foster, F. Deledalle, A. Mitani, T. Kimura, K. B. Kim, T. Okachi, T. Kirchartz, J. Oguma, K. Miyake, J. R. Durrant, *Adv. Energy Mater.* 4 (2014) doi: 10.1002/aenm.201400311.
- 40 L. Lu, T. Xu, W. Chen, J. M. Lee, Z. Luo, I. H. Jung, H. I. Park, S. O. Kim, L. Yu, *Nano Lett.* 13 (2013) 2365-2369.
- 41 H. Zang, Z. Xu, B. Hu, *J. Phys. Chem. B* 114 (2010) 5704-5709.
- 42 T. Leijtens, S. D. Stranks, G. E. Eperon, R. Lindblad, E. M. Johansson, I. J. McPherson, H. Rensmo, J. M. Ball, M. M. Lee, H. J. Snaith, *ACS nano* 8 (2014) 7147-7155.
- 43 A. Abate, M. Saliba, D. J. Hollman, S. D. Stranks, K. Wojciechowski, R. Avolio, G. Grancini, A. Petrozza, H. J. Snaith, *Nano Lett.* 14 (2014) 3247-3254.
- 44 H.-S. Kim, I. Mora-Sero, V. Gonzalez-Pedro, F. Fabregat-Santiago, E. J. Juarez-Perez, N.-G. Park, J. Bisquert, *Nat. commun.* 4 (2013) 2242.
- 45 V. Roiati, E. Mosconi, A. Listorti, S. Colella, G. Gigli, F. De Angelis, *Nano Lett.* 14 (2014) 2168-2174.
- 46 P. Schulz, E. Edri, S. Kirmayer, G. Hodes, D. Cahen, A. Kahn, *Energy Environ. Sci.* 7 (2014) 1377-1381.
- 47 J. Szmytkowski, W. Stampor, J. Kalinowski, Z. Kafafi, *Appl. Phys. Lett.* 80 (2002) 1465-1467.
- 48 C. L. Braun, *J. Chem. Phys.* 80 (1984) 4157-4161.
- 49 D. Veldman, O. Ipek, S. C. Meskers, J. r. Sweelssen, M. M. Koetse, S. C. Veenstra, J. M. Kroon, S. S. v. Bavel, J. Loos, R. A. Janssen, *J. Am. Chem. Soc.* 130 (2008) 7721-7735.
- 50 V. Mihailetschi, L. Koster, J. Hummelen, P. Blom, *Phys. Rev. Lett.* 93 (2004) 216601.
- 51 N. C. Miller, R. Gysel, C. E. Miller, E. Verploegen, Z. Bailey, M. Heeney, I. McCulloch, Z. Bao, M. F. Toney, M. D. McGehee, *J. Polym. Sci. B Polym. Phys.* 49 (2013) 499-503.
- 52 T. M. Burke, M. D. McGehee, *Adv. Mater.* 26 (2013) 1923-1928.
- 53 B. Bernardo, D. Cheyns, B. Verreert, R.D. Schaller, B.P. Rand, N.C. Giebink. *Nat. Commun.* 5 (2014) 3245.