

Addressing dynamic photovoltaic processes at electrode:active layer and donor:acceptor interfaces in organic solar cells under device-operating conditions

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This article presents our experimental studies to unravel the dynamic photovoltaic processes occurring at donor:acceptor (D:A) and electrode:active layer (E:A) interfaces under device-operating conditions by using two unique magneto-optical measurements, namely photo-induced capacitance and magnetic field effect measurement. First, we have found that a higher surface polarization of dielectric thin film can decrease the surface charge accumulation at E:A interface. The photo-induced capacitance results indicate that dielectric thin film plays a crucial role in the charge collection in generating photocurrent in organic solar cells. Second, our experimental results from magnetic field effect show that the binding energies of charge transfer (CT) states at D:A interface can be evaluated by using the critical bias required to completely dissociate the CT states. This is the first experimental demonstration that the binding energies of CT states can be measured under deviceoperating conditions. Furthermore, we use our measurement of magnetic field effect to investigate the most popular organic photovoltaic solar cells, organometal halide perovskite photovoltaic devices. The results of magneto-photoluminescence show that the photogenerated electrons and holes are inevitably recombined into electron-hole pairs through a spin-dependent process in the perovskites. Therefore, using spin polarizations can present a new design to control the photovoltaic loss in perovskites-based photovoltaic devices. Also, we found that introducing D:A interface can largely affect the bulk charge dissociation and recombination in perovskite solar cells. This indicates that the interfacial and bulk photovoltaic processes are internally coupled in developing photovoltaic actions in perovskite devices. Clearly, these magneto-optical measurements show a great potential to unravel the deeper photovoltaic processes occurring at D:A and E:A interfaces in both organic bulk-heterojunction and perovskite solar cells under device-operating conditions.

electrode interface, donor–acceptor interface, dielectric layer, charge transfer states

1 Introduction

Organic photovoltaic devices have attracted great attention for the past two decades due to the unique features such as mechanical flexibilities, facile materials processing, and low costs. Recent research developments have demonstrated high photovoltaic efficiencies with the values around 10%

in polymer-based organic solar cells [1–7]. Recently, perovskite materials have shown surprisingly high photovoltaic efficiencies reaching 20% [8–12]. These recent fascinating developments have brought a fundamental demand: revealing deeper internal photovoltaic processes occurring at dynamic donor:acceptor (D:A) and electrode:active layer (E:A) interfaces under device-operating conditions. Clearly, investigating deeper internal photovoltaic processes can provide critical understanding of the key factors controlling the

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dynamic D:A and E:A interfaces to further advance the research and development of organic solar cells.

In both organic bulk-heterojunction and perovskite solar cells, recent advancements have shown that using charge-transporting films or buffer layers from oxides or electrolytes can lead to significant enhancements on photovoltaic efficiencies in organic solar cells [13–18]. These recent advancements indicate that the electrode interface plays an important role in enhancing photovoltaic performance. Recently, the photo-induced capacitance experimental studies have shown that photogenerated charge carriers can be inevitably accumulated at E:A interface upon charge transport to respective electrodes [19,20]. Obviously, the charge accumulation can generate a photovoltaic loss when an organic solar cell is under operation. The results of photo-induced capacitance measurement indicate that the charge accumulation exists at E:A interface of the device. On one hand, the photo-induced capacitance measurement results also suggest that using high dielectric constant interlayer can effectively modify the surface charge accumulation, and then increase the device performance. The early experimental studies have found three specific effects from dielectric thin films in organic solar cells. First, dielectric thin film can affect the vertical distributions of donor and acceptor components within respective surface areas due to strong dielectric interaction and surface energy, and consequently enhances the electron and hole transport channels [13,14,21,22]. Second, a high dielectric thin film can form interfacial dipoles with electrodes, leading to a modification on electrode work function and energy alignment [23–29]. Third, using dielectric thin film can change the optical field distribution of incident electromagnetic waves inside a photovoltaic film to increase photon absorption [15,30]. Clearly, controlling charge accumulation by using high dielectric interlayer presents a new mechanism to improve photovoltaic performance in organic solar cells.

In general, the D:A interface provides three necessary photovoltaic functions: (i) dissociating photogenerated excitons, (ii) transporting the dissociated electrons and holes, and (iii) establishing photovoltage through the light–electricity energy conversion. It should be noted that the dissociation inevitably leads to positively charged donor and negatively charged acceptor at D:A interface. Consequently, the Coulomb attraction can occur between the dissociated electrons located in acceptor and the dissociated holes located in donor, leading to the formation of electron–hole pairs, namely charge transfer (CT) complexes, at the D:A interface [31–38]. More importantly, this unavoidable Coulomb attraction can cause certain binding energies for the CT complexes at D:A interface. Essentially, dissociating the CT complexes is a critical issue in generating photocurrent and photovoltage. Therefore, revealing the key parameters controlling the binding energies at D:A interface is an important research topic toward the further advancement in organic solar cells. Here, mixing an electron–donor photo-

voltaic polymer with electron–acceptor molecules can lead to three different phases: donor phase, acceptor phase, and mixed donor and acceptor phase in bulk-heterojunctions [39]. The intermolecular D:A interfaces can be formed both within mixed donor and acceptor phase and between the donor and acceptor phases. Many previous studies have shown that the CT states also play an important role to effect open circuit voltage (V_{oc}) and short-circuit current (J_{sc}) [40,41]. Here, we combine magnetic field effects of photocurrent (MFE_{PC}) with an external electric field, as an experimental tool, to monitor the binding energies at the D:A interfaces, namely V-MFE_{PC}. MFE_{PC} were originally observed in pristine organic materials at low-field regime (<100 mT) in the 1970s [42–44]. The early studies have shown that a magnetic field can change the photoconduction with positive or negative sign in organic materials. Based on the early studies, we found that the charge dissociation at D:A interfaces in organic solar cells can show the MFE_{PC} at high-field regime (>100 mT) [45]. Specifically, the D:A interfaces can inevitably form the CT states, due to the Coulomb attraction, with singlet and triplet spin states in organic solar cells under device-operating conditions. A magnetic field (>100 mT) can modify the singlet/triplet ratio in CT states by disturbing the singlet–triplet intersystem crossing through spin mixing [46]. Because the singlets and triplets have high and low dissociation rates due to the different ionic properties of their wavefunctions [47–50], magnetically modifying the singlet/triplet ratio in CT states at D:A interfaces can then cause a change in photocurrent, leading to MFE_{PC} at high-field regime (>100 mT). Therefore, the MFE_{PC} at high-field regime can be used to monitor the charge dissociation at D:A interfaces under device-operating conditions. Furthermore, we found that combining the MFE_{PC} with an external electric field provides an *in situ* measurement to evaluate the binding energies at the D:A interfaces during the charge dissociation in the generation of photocurrent. In this *in situ* measurement, an external electric field can facilitate the dissociation of the CT states at D:A interfaces by overcoming the Coulomb attraction. As a consequence, an external electric field can decrease the density of CT states at D:A interfaces and reduces the signal amplitude in the MFE_{PC}. As a result, the critical electric field required to cease MFE_{PC} can indicate the binding energies at D:A interfaces in organic solar cells. Besides polymer/fullerene solar cells, magneto-optical measurements can also be used to study perovskite solar cells, such as the nature of photoexcited states as well as the critical photovoltaic processes. Our recent works have revealed the spin-dependent photoexcited states in perovskite materials based on the magneto-photoluminescence results. This magneto-photoluminescence can be associated with the spin-dependent recombination process in perovskite materials. Clearly, magneto-optic measurements can provide a deeper understanding of the internal photovoltaic processes in perovskite solar cells at device-operating conditions.

2 Methods

The current-voltage (I - V) characteristics were measured by using Keithley 2400 Source Meter with Sunlight Simulator (Thermal Oriel 96000 300 W from Newport) with photoexcitation intensity of 100 mW/cm^2 . The photo-induced capacitance measurements were performed under alternating voltage of 50 mV at 1 kHz by using a dielectric spectrometer (Agilent E4980A LCR, USA) (Figure 1). The MFE_{PC} were recorded by measuring the short-circuit current as a function of magnetic field under either simulated sunlight or 532 nm laser illumination. The MFE_{PC} amplitude is defined as $\frac{I_{\text{B}} - I_0}{I_0}$, where I_{B} and I_0 are the photocurrents with and without applied magnetic field at short-circuit condition. The binding energies of CT states at D:A interfaces were evaluated by combining MFE_{PC} with an external electric field (applied by using Keithley 2400 Source Meter). All measurements were performed under nitrogen gas atmosphere at room temperature.

3 Results and discussion

3.1 Addressing E:A interface to control charge accumulation and collection at respective electrodes

Figure 2 shows the photo-induced capacitance characteristics for the PTB7:PCBM-based organic solar cell device at different light illumination intensities up to 1 sun (100 mW/cm^2) with device structure of ITO/PEDOT:PSS/PTB7:PCBM/Ca/Al. The photo-induced capacitance measurements indicate the following three typical information. First, when the applied bias is increased, the device capacitance under photoexcitation increases before V_{peak} (as shown in Figure 2) point and then decreases after the V_{peak} point. This means that the V_{peak} corresponds to the critical voltage at which the charge carriers begin to inject into photovoltaic film. Second, the device capacitance at zero bias point in-

creases with increasing photoexcitation intensity. This suggests that photogenerated carriers under higher light intensity lead to more charge accumulation on the surfaces of photovoltaic films. Third, when the photoexcitation intensity is increased, the V_{peak} in the photo-induced capacitance characteristics shifts to a lower value. This indicates that increasing the surface accumulation of photogenerated carriers can lower the critical voltage V_{peak} required to initiate the charge injection into the bulk photovoltaic film. The reduction on V_{peak} due to the accumulation of photogenerated carriers can be discussed as follows. The dark injection barrier in the metal-semiconductor interface can be described by the following equation [51]:

$$n_i = N_t \exp\left(-\frac{\phi_i}{k_{\text{B}}T}\right) \quad (1)$$

where the n_i is the surface charge density, N_t is the volume density of molecular sites, and ϕ_i is the potential barrier at the interface between the active layer and the electrode. Clearly, the higher charge density will lead to a lower potential barrier. It should be noted that the injected charge carriers at photovoltaic layer/electrode interfaces under V_{peak} condition contain both photogenerated carriers from photovoltaic layers and dark carriers from electrodes. As a result, increasing the photogenerated charge carriers at photovoltaic layer/electrode interfaces can directly decrease the surface potential barrier at which the V_{peak} initiates charge injection. Clearly, the V_{peak} shift with light intensity provides an experimental evidence to indicate that the photogenerated charge carriers are inevitably accumulated at photovoltaic layer/electrode interfaces.

Now, we start to investigate the photovoltaic effect of dielectric interlayer in organic solar cells. Figure 3 shows the surface polarization measurement for different dielectric electron collection layers (ECLs) at different applied biases such as poly[(9,9-bis(3-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] [PFN (blue line)], TiO_x (green line), and ZnO (red line) based on the device structure of ITO/ECL(50 nm)/Au, respectively. We should

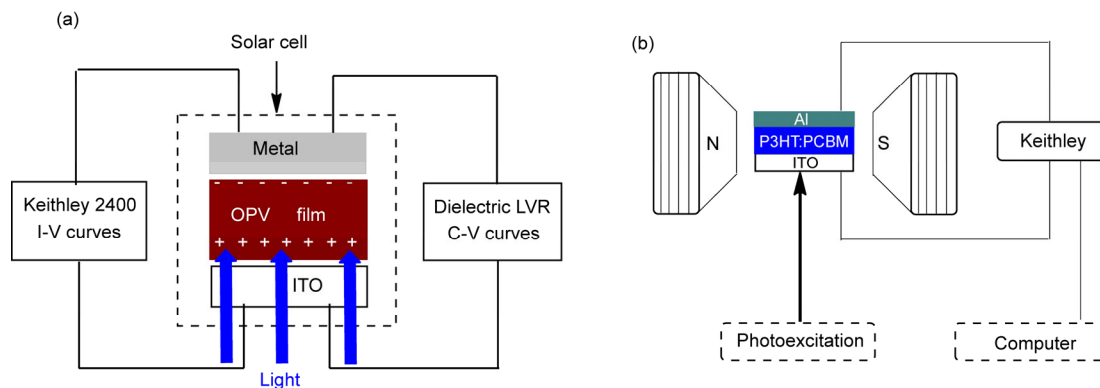


Figure 1 The diagram of the experimental setup for (a) photo-induced capacitance measurement and (b) V - MFE_{PC} measurement.

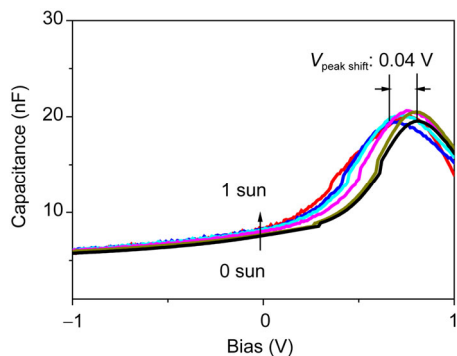


Figure 2 The classic plot of light-assisted capacitance measurement [20].

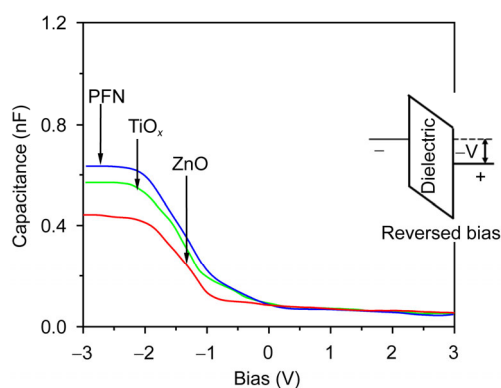


Figure 3 Dielectric property measurements with device structure of ITO/ECL/Au under a sweeping bias from -3 V to 3 V [20].

note that the capacitance of a thin film device is essentially related to the surface polarization. The results of Figure 3 indicate that the PFN device shows a relative higher capacitance than both TiO_x and ZnO at the reverse bias of -3 V. We can see from the schematic band diagram (Figure 3 inset) that a reverse bias can electrically polarize the dielectric film without enabling charge injection. Therefore, at reverse bias, a larger capacitance should correspond to a higher surface polarization [52]. Based on this analysis, our capacitance data suggest that the PFN has a higher surface polarization than TiO_x and ZnO. By combining the I - V characteristic and surface polarization results, we can see that dielectric properties of ECLs play an important role in enhancing photovoltaic process.

Figure 4 shows the photo-induced capacitance characteristics at different photoexcitation intensities up to 100 mW/cm^2 (1 sun condition) for OPV cells with different ECLs. More importantly, we can see in Figure 4 that different dielectric layers with different surface polarizations correspond to different V_{peak} shifts. By combining the results from Figure 3, we can see that the capacitance value increases from ZnO to TiO_x and PFN based on a single-layer design. Because the capacitance is essentially related to the surface polarization of a dielectric layer in the single-layer devices, we can thus suggest that the surface polarization increases from ZnO to TiO_x and PFN. Therefore, we can

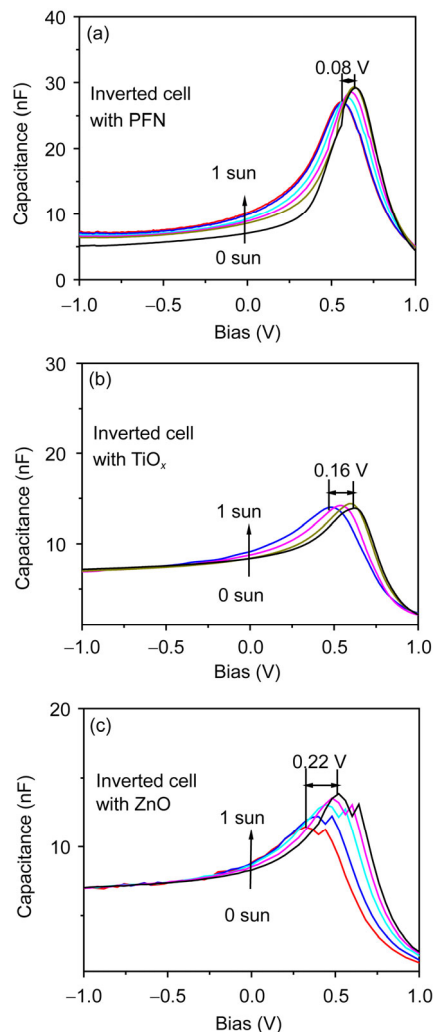


Figure 4 Photo-induced capacitance characteristics at different photoexcitation intensities ranging from 0 mW/cm^2 to 100 mW/cm^2 for the inverted devices with three different dielectric constants of ECLs based on the common photovoltaic PTB7:PCBM composite with ITO/ECL/PTB7:PCBM/MoO₃/Ag architecture. (a) PFN, (b) TiO_x , and (c) ZnO [20].

argue from our V_{peak} shift shown in Figure 4 that increasing the surface polarization of a dielectric layer can lead to a decrease in the surface accumulation of photogenerated carriers toward the effective charge collection in organic solar cells. Figure 5 shows the current-voltage (I - V) characteristics for the inverted devices with different electron-collecting dielectric layers and the same hole-collecting layer (MoO_3) based on the common PTB7:PCBM in the inverted devices. It could be seen that the inverted device with the PFN as an ECL yields a higher power conversion efficiency (PCE) of 8.7% compared with the devices with TiO_x (PCE: 7.3%) or ZnO (PCE: 6.6%) as ECL, which is equivalent to 19% enhancement and 32% enhancement in efficiency. Obviously, the higher interfacial polarization can be formed by introducing high dielectric interlayer which can lower the surface charge accumulation, and then leads to a higher PCE in organic solar cells.

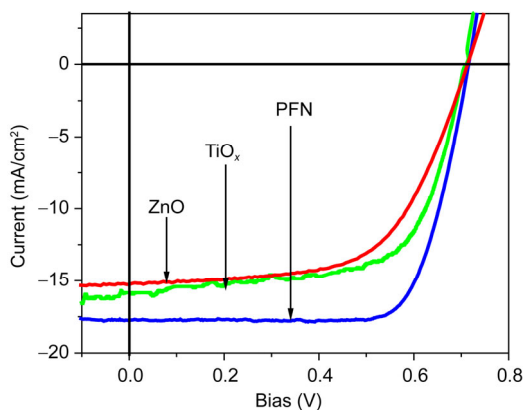


Figure 5 *I-V* characteristics for inverted PTB7:PCBM devices with different ECLs under the AM 1.5G condition (100 mW/cm^2) [20].

3.2 Addressing D:A interface to control electron-hole binding energies

The bounded intermolecular electron-hole pairs, namely CT states, have been proved as an important mediated state to significantly affect the photovoltaic performance in organic solar cells [40,41]. In particular, the binding energies of CT states (E_{bct}) at D:A interfaces in polymer/fullerene bulk-heterojunction solar cell have been recognized as the most important parameter to affect the formation and dissociation rates of CT states. Our previous work has demonstrated that E_{bct} is essentially determined by two components of the free energy of electron-hole pairs: (i) potential energy, resulted from Coulomb attraction, is determined by dielectric constant of the medium and charge separation distance at D:A interfaces and (ii) kinetic energy, resulted from electric drifting, is determined by the built-in electric field (F_{bi}) and charge mobilities (μ_e and μ_h) [53]. Notably, magnetic field effect would be expected to evaluate E_{bct} at D:A interfaces based on the following well-accepted points: on one hand, CT states can be formed with both singlet and triplet con-

figurations in organic semiconductors due to electron spin multiplicities. The external magnetic field can change the ratios of singlet to triplet via perturbing the intersystem crossing (as shown in Figure 6(a)). Consequently, the change of singlet and triplet ratio would give rise to the photocurrent change due to the high and low dissociation rates for singlet and triplet, respectively (as shown in Figure 6(b)). On the other hand, an external electric field can interact with the internal built-in electric field to compete with Coulomb attraction which can promote the dissociation of CT states. Clearly, by combining the magnetic field effect on photocurrent with external electric field, namely V-MFEpc, a critical electric field could be obtained to evaluate E_{bct} .

Figure 7(a) shows positive signals of MFEpc in ITO/PEDOT:PSS/P3HT:PCBM/Al device with different blend ratios between P3HT and PCBM. This positive MFEpc signal can be suggested as the signature of CT complex states formed from dissociated electrons and holes at the P3HT-PCBM interfaces [45]. It can be seen that the amplitude of this high-field magnetic field-dependent photocurrent depends on the PCBM weight ratio in the P3HT:PCBM solar cell. The decreasing of MFEpc signal upon increasing the PCBM weight ratio from 0.2 to 0.8 shows that the density of formed CT complexes decreases with increasing the PCBM weight ratio in bulk-heterojunction organic solar cells. Moreover, increasing the PCBM concentration up to 1:2 weight ratio of P3HT:PCBM leads to an increase of positive MFEpc. This change in the amplitude of positive MFEpc can be related to the reduction of effective donor-acceptor interaction due to more significant PCBM aggregation at higher concentration. Clearly, the 1:0.8 weight ratio of P3HT:PCBM yields a lowest density of CT states. This low density of CT complexes corresponds to a higher fill factor of 0.61 in the ITO/P3HT:PCBM/Al solar cell (Figure 7(b)). Based on the results from Figure 7, we can make a solid argument that the CT states are formed at D:A

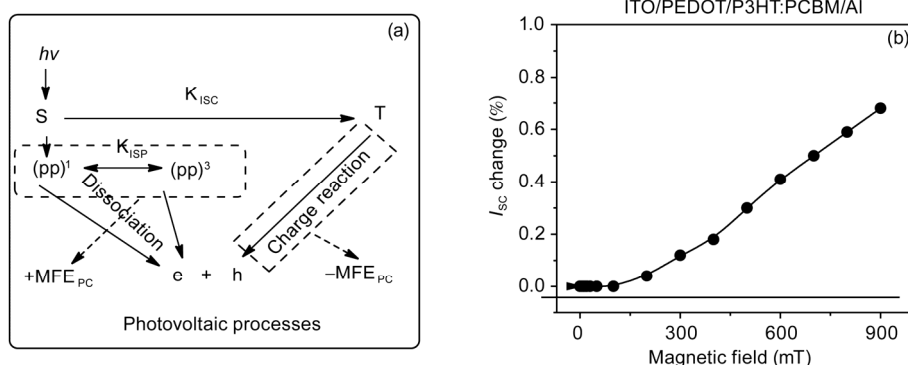


Figure 6 (a) Photocurrent-generation channels and (b) magnetic field effects of photocurrent MFE_{PC} in bulk-heterojunction P3HT:PCBM solar cell [53]. Photocurrent-generation channels: dissociation of polaron pairs, dominated by singlet excitons, and exciton-charge reaction, dominated by triplet excitons. S and T represent photoexcited singlet and triplet excitons. $(\text{PP})^1$ and $(\text{PP})^3$ are intermolecular singlet and triplet polarons. K_{ISC} and K_{ISP} are intersystem crossing in excitonic and polaron-pair states. $+\text{MFE}_{\text{PC}}$ and $-\text{MFE}_{\text{PC}}$ are positive and negative components in magnetic field effects of photocurrent in low-field regimes. (b) MFE_{PC} for ITO/PEDOT:PSS/P3HT:PCBM/Al solar cell. The weight ratio of P3HT:PCBM is 1:0.8. The MFE_{PC} for pristine P3HT device (ITO/P3HT/Al) is shown as an inset.

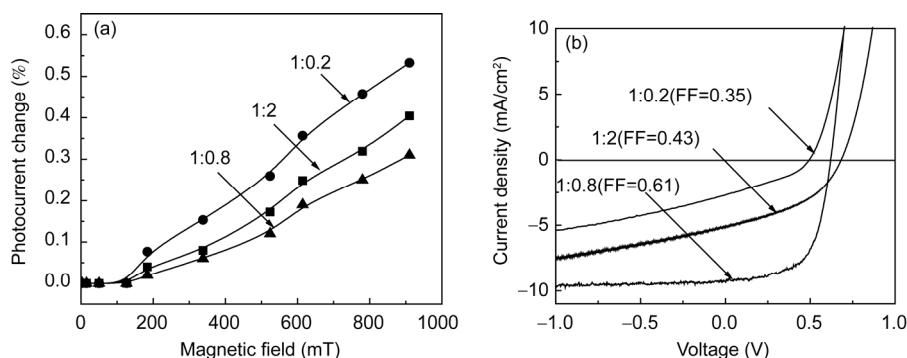


Figure 7 (a) High-field magnetic field effects of photocurrent for different P3HT:PCBM weight ratios. (b) Photocurrent–voltage characteristics for ITO/PEDOT:PSS/P3HT+PCBM/Al solar cells with different P3HT:PCBM weight ratios. FF: fill factor [45].

interface and show magnetic field-dependent phenomenon.

Now we discuss the binding energies of CT states at the D:A interface in P3HT:PCBM-based organic solar cell. Figure 8 shows the V-MFE_{PC} measurements of the P3HT:PCBM-based organic solar cell. It was observed that the MFE_{PC} can be significantly increased in organic solar cells by reducing the dissociation of photoexcited states around short-circuit condition when a forward electric field is applied to cancel internal electric field [50]. This result implies that the density of photoexcited states responsible for MFE_{PC} can be largely modulated by external electric field. Here, we use reverse electric field to enhance the dissociation of CT states by reducing the coulombic attraction force of CT states and consequently to decrease the MFE_{PC} amplitude. We should note that the measurement of V-MFE_{PC} can provide information on the binding energies of CT states. The amplitude cancellation of high-field MFE_{PC} at 900 mT shows that the applied electric field of -0.5 V reverse bias is the critical voltage to dissociate all CT states at D:A interface in the P3HT:PCBM solar cell. As a result, we can assign this 0.5 V critical voltage to the binding energies of CT states at D:A interfaces. Clearly, the V-MFE_{PC} measurement, a new method which combines optical–magneto-electrical properties, shows a great potential to investigate the physics meaning of organic solar cell.

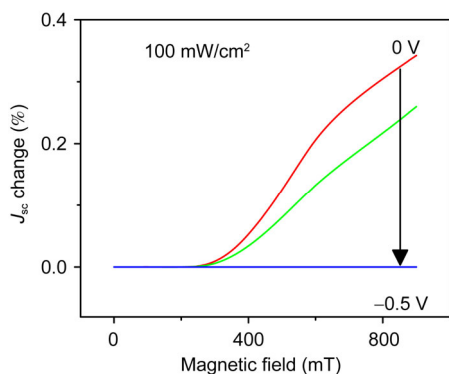


Figure 8 Magnetic field effects on photocurrent measured at different external electric fields in the ITO/PEDOT:PSS/P3HT:PCBM/Al device under simulated sunlight of a 100 mW/cm^2 intensity.

3.3 Magneto-optical studies on perovskite solar cells

Organometal trihalide perovskite materials have recently become extremely attractive photovoltaic candidates to develop high-efficiency solar cells. The materials processing and device engineering have led the power conversion efficiencies to quickly increase from 3% to 20% with facile solution-processable features [8–12]. The early studies in 1991 from Japanese scientists have observed a magneto-optic phenomenon from methylammonium lead triiodide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$): a high magnetic field (up to 40 T) can decrease the optical absorption intensity in $\text{CH}_3\text{NH}_3\text{PbI}_3$ at low temperature (4.2 K) [54]. However, the fundamental mechanisms have remained still unclear. However, this experimental observation can indeed suggest a fundamental possibility to develop magneto-optic properties from organolead trihalide perovskites. On the other hand, magneto-optic properties can be used as a unique experimental tool to reveal the polarization, spin, and energy parameters in controlling useful and nonuseful photovoltaic processes in perovskite solar cells. Recently, we have performed magneto-optical studies on the internal photovoltaic processes in perovskite solar cells by using photoluminescence (PL) and magneto-photoluminescence. We have found, for the first time, that the perovskites can exhibit magneto-photoluminescence at low field (<1 T) and room temperature (Figure 9(a)). This experimental finding indicates that the photoexcited states are spin dependent in this type of perovskites. In particular, the recombination of photogenerated electrons and holes undergoes a spin-dependent process. This presents a new method to control the charge recombination by using spin polarizations in perovskite solar cells. Furthermore, we have observed in Figure 9(a) that introducing electron acceptor–PCBM interface can appreciably decrease the signal amplitude of magneto-photoluminescence. This experimental observation provides the first evidence that the D:A interface can affect the bulk recombination of photogenerated electrons and holes in the perovskite solar cells under device-operating conditions. Furthermore, we have found that introducing the D:A interface not only quenches the PL but also largely decreases the

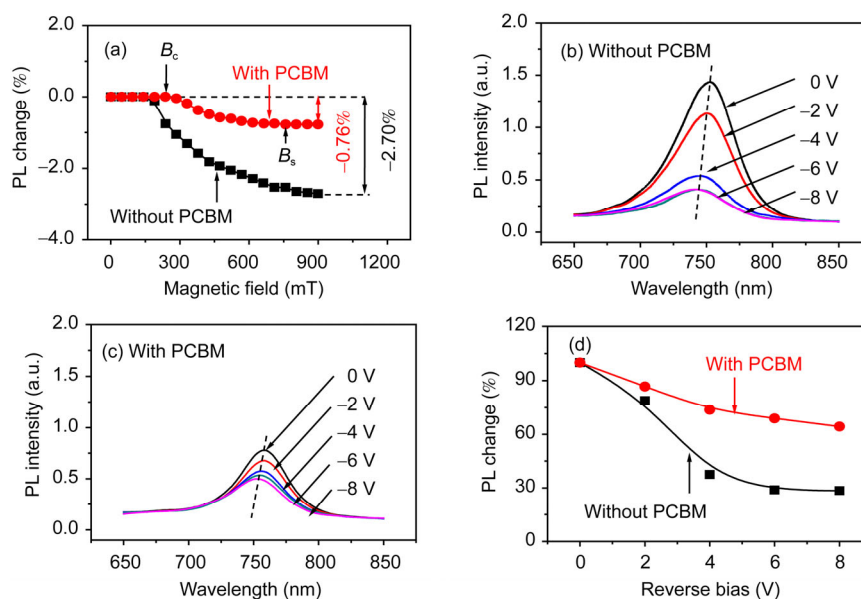


Figure 9 Magneto-optical studies on perovskite solar cells: (a) Magneto-photoluminescence from $\text{CH}_3\text{NH}_3\text{PbI}_3$ single layer and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ double layer under the photoexcitation of 532 nm CW laser. (b) Electric field-dependent PL for $\text{CH}_3\text{NH}_3\text{PbI}_3$ single-layer sample (ITO/ $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Al}$). (c) Electric field-dependent PL for $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ sample (ITO/ $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}/\text{Al}$). (d) PL quenching for both single-layer and double-layer samples under photoexcitation of xenon lamp at 530 nm and with the reverse bias from 0 V to 8 V.

PL dependence of electric field (Figure 9(b–d)). This experimental observation indicates that the D:A interface forms an interfacial electric field to enhance the charge dissociation toward the generation of photocurrent in perovskite solar cells. It has been revealed that the PL from perovskite materials arises from the recombination process [55]. Here, our magneto-photoluminescence results provide a solid evidence that the charge recombination can inevitably occur through a spin-dependent process in perovskite materials. Especially, introducing D:A interface can lead to interfacial dipoles and consequently influences the bulk charge recombination and dissociation in perovskite materials. Clearly, our magneto-optic studies can provide a deeper understanding of improving the internal photovoltaic processes in perovskite solar cells.

4 Conclusions

It has been experimentally found that both E:A and D:A interfaces play crucial roles in the photovoltaic processes in organic solar cells. Here, we present that the photo-induced capacitance and V-MFEpc measurements provide effective *in situ* tools to investigate the E:A and D:A interfaces under device-operating conditions. First, the photo-induced capacitance can show the surface charge accumulation at E:A interface by evaluating the V_{peak} shift under different photoexcitation intensities. Furthermore, using high dielectric interfacial layers can reduce the charge accumulation at E:A interface via the high interface polarizations. In particular, the interface polarization can provide an extra driving force

to extract the accumulated space carriers from the organic active layer to the respective electrodes, leading to a higher photocurrent. Second, the V-MFEpc can be used as a unique method to estimate the binding energies of CT states at D:A interface in the generation of photocurrent. Specifically, the competition between electrical drifting and Coulomb attraction determines the formation and dissociation probabilities of electron–hole pairs in the CT states at the D:A interfaces. Furthermore, in perovskite solar cells our magneto-optical studies have revealed that (i) the recombination of photogenerated electrons and holes inevitably occurs through spin-dependent process and (ii) the D:A interface can largely affect the bulk charge dissociation and recombination in generating photovoltaic actions. Clearly, our magneto-optical measurements provide unique *in situ* experimental tools to address both D:A and E:A interfaces in organic bulk-heterojunction and perovskite solar cells under device-operating conditions.

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