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Magnetic field effect of the singlet fission reaction in tetracene-based diodes

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ABSTRACT

We investigate the magnetophotocurrent (MPC) response in tetracene-based diodes and attribute the initially decreasing and then increasing MPC responses to the feature of the singlet fission (SF) reaction (a magnetic field sensitive process) as modulated by the applied magnetic field in the tetracene active layer. The SF reaction is further characterized by the magnetophotoluminescence (MPL) measurement of the tetracene film, in which the variation of MPL is correlated with the change of MPC response in the device. However, the SF reaction of the singlet excitons in the tetracene would compete with the separation of the opposite charge carriers at the donor/acceptor interfaces by depositing the fullerene (C_{60}) on the tetracene active layer to yield a planar heterojunction. Our results indicate that the charge separation is more effective than the SF reaction. The dissociation and the charge reaction processes of the charge transfer complexes at donor/acceptor interfaces dominate the photocurrent as well as MPC response in tetracene/C_{60}-based diodes.

1. Introduction

In recent years, the study of magnetic field effects (MFEs) in organic semiconductor devices has been subjected to an increasing attention [1–5]. An external magnetic field changes the intersystem crossing process of the singlet and triplet polaron pairs; moreover, the different binding energies and lifetimes of singlet and triplet excited states yield the different electric properties and result in the changes of photocurrent, electroluminescence, photoluminescence and efficiency of those devices [4–7]. Until now, most contemporary models can be divided into two major classes; bipolaron-based and exciton-based model [8–13]. As proposed by the bipolaron-based model, there is a competition between the formation of the bipolarons and the hopping transport of charge carriers to the empty electronic site [8–10]. This model also suggests that the applied magnetic field modulates the mobility of charge carriers and current density. In the exciton-based model, some researchers claimed that the observation of the MFE after the “turn on” voltage of the electroluminescence in the organic light-emitting diode and investigated the correlation between excited states with MFE of the devices [11]. Additionally, there are numbers of different models associated with the exciton-based model, such as electron-hole pairs model [12,13], triplet-polaron pairs model [11,14], triplet-triplet annihilation model [15,16], etc. Many of the models suggest that MFE of the organic conjugated molecules involves the formation of excited states as modulated by the applied magnetic field [17,18].

According to the study by Frankevich *et al.* [1], the external magnetic field would change the population of singlet/triplet excited states through the intersystem crossing of the long range electron-hole pairs, called the polaron pairs (PPs). However, in addition to the intersystem crossing between singlet PPs ($(PPs)_1$) with triplet PPs ($(PPs)_3$), the singlet fission (SF) reaction is another pathway to modulate the population of singlet and triplet excited states. SF involves the conversion of one molecule in the singlet excited state with another one in the ground state into two triplet excited molecules, which feasibly occurs when the band gap of the singlet excited state is approximately twice the magnitude of the triplet state [19,20]. Merrifield *et al.* [21] have proposed that there is a strong SF reaction in anthracene and tetracene molecules, in which the SF reaction is characterized by the changes of the photoluminescence (PL) spectra under the external magnetic field (magnetophotoluminescence (MPL) measurement). Recent studies also indicated that the applied magnetic field changes the SF rate as well as magnetophotocurrent (MPC) or MPL [22–24] responses of devices. The influence of applied magnetic field on the SF reaction would be an important parameter to modulate overall MPC responses in anthracene- and tetracene-based devices.

In this manuscript, we investigate the MPC response in the tetracene-based diodes and observe the initially decreasing and then increasing magnitude of MPC response at the low and high magnetic

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field, respectively, which could be the feature that is associated with the SF reaction (a magnetic field sensitive process) in the tetracene active layer. The SF reaction is further characterized by the MPL measurement of the tetracene film. The variation of MPL is correlated with the change of MPC response in the device. Nevertheless, depositing the fullerene (C_{60}) on the tetracene active layer to yield a planar heterojunction (PHJ) separates the opposite charge carriers at the donor/acceptor interfaces, which is a competing process with the SF reaction for the excited molecules. Our results indicate that the charge separation at donor/acceptor interfaces is more effective than the SF reaction. As a consequence, the dissociation and the charge reaction processes of the charge transfer complexes at the tetracene/C_{60} (donor/acceptor) interfaces dominates the generation of the photocurrent as well as MPC response in tetracene/C_{60}-based diodes.

2. Experimental section

2.1. Device fabrication

The device comprises of a glass/indium-tin-oxide (ITO) (RITEK Corp.) with a sheet resistance of 15 Ω/square as a substrate. The poly (3,4-ethylenedioxythiophene):poly(styene-sulfonate) (PEDOT:PSS; Bayron P, Bayer AG, Germany) was coated on the substrate at a speed of 4000 rpm as the hole transport layer. The glass/ITO/PEDOT:PSS substrate was then annealed at 150 °C for 25 min to remove the residue of water molecules. The active layer, the tetracene (60 nm, Shifeng Technology, Taiwan) or the tetracene/C_{60} (40 nm/40 nm) (> 99.5%, Solenne b.v.), was deposited on the substrate by a vacuum thermal evaporator at a pressure of 3×10^{-6} torr. The bathocuproine (BCP) (10 nm) (Aldrich) was used as an exciton blocking layer to reduce the exciton losses by the metal electrode (Al) [25,26]. Without BCP buffer layer, the magnitude of photocurrent and the MPC of the device are low. BCP and Al (100 nm) were then deposited on the top of the active layer. The configuration of device was glass/ITO/PEDOT:PSS/active layer/BCP (10 nm)/Al (100 nm). The active area of the device was 6 mm^2. All steps for the fabrication were performed in a nitrogen-filled glove box with both moisture and oxygen levels below 1 ppm except for the preparation of the PEDOT:PSS layer.

2.2. MPC and MPL measurements

For measuring MPC responses, the device was mounted on the stage (inside a vacuum tube, $\sim 10^{-3}$ torr) between the two poles of an electromagnet and the direction of the applied magnetic field was perpendicular to the current flow of device. The current density-voltage (*J-V*) curves were measured using a sourcemeter (Keithley 2611A). The photocurrent was measured by illuminating the device with a halogen light (LSH 100). To minimize the influence of drift effect under the electric bias, MPC curves were averaged as elsewhere [27]. The MPC ratio is defined as $MPC = \Delta I(B)/I(0) = (I(B)-I(0))/I(0)$, where $I(B)$ is the photocurrent under the applied magnetic field, $I(0)$ is the photocurrent without any applied magnetic field, and $\Delta I(B)$ is the changes in photocurrent with and without the applied magnetic field. The interval for the change of the magnetic field in MPC measurement is 20 Oe. There are totally 100 data points between -1000 and 1000 Oe in our measurement. In measuring PL and MPL, the 405 nm laser was used as the photoexcitation beam and PL intensity was recorded by ihR550 spectrometer. The samples were placed between the electromagnet poles and an optical fiber was used to collect the spectrum. MPL ratio is defined as $MPL = (PL(B)-PL(0))/PL(0)$, where $PL(B)$ and $PL(0)$ are the intensities of the PL with and without the applied magnetic field, respectively. The interval for the change of the magnetic field in MPC measurement is 100 Oe. For both MPC and MPL measurement, the device was encapsulated by a glass substrate with UV-curable epoxy to avoid the direct contact of the device with atmosphere during the measurement.

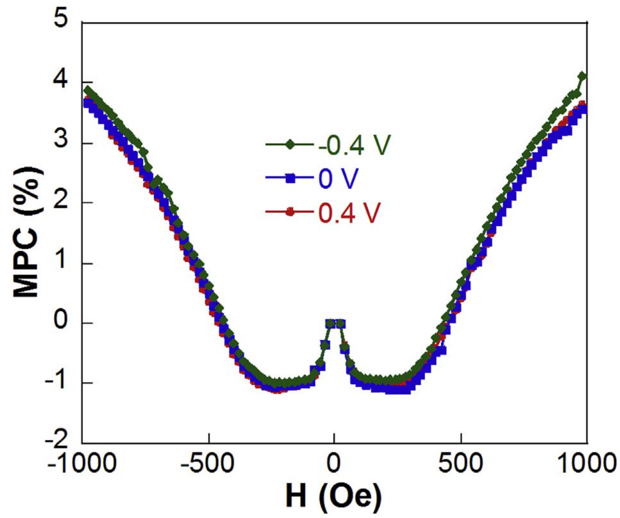

Fig. 1. MPC responses of ITO/PEDOT:PSS/tetracene/BCP/Al device under illumination at different voltages (−0.4 V, 0 V, and 0.4 V).

3. Results and discussion

Fig. 1 shows the MPC responses for ITO/PEDOT:PSS/tetracene/BCP/Al device under illumination at different voltages. We observe the initially decreasing (negative component) and then increasing (positive component) magnitude of MPC response at the low and high magnetic field, respectively. No apparent MPC response was detected for devices without illumination. At the first glance, we may attribute the variations of the MPC responses in Fig. 1 to the modulation of PPs by the applied magnetic field from the exciton-based model reported in the previous studies [18,28]. However, it should be noted that the device biased at various voltages exhibits a similar curve shape of the MPC response. Generally, the applied electric bias would modulate the dissociation of PPs to change the magnitude and curve shape of MPC responses. The observation in Fig. 1 is different from the results in the previous studies [4,18,29]. There should be another magnetic-field sensitive process to dominate MPC response herein. The SF reaction among the excited tetracene molecules is a magnetic-field sensitive process [24] and could be correlated with the modulation of the MPC response in tetracene-based devices.

Fig. 2(a) shows the possible routes for relevant particles transfer in the organic molecules. In addition to the intersystem crossing ($K_{ISC}(B)$) between $(PPs)_1$ and $(PPs)_3$ (a magnetic-field sensitive process), the SF reaction (SF(B)) is another magnetic-field sensitive process that can change the distribution of singlet and triplet excited states [30]. Since the radiative recombination of singlet excitons yields the PL, the modulation of the SF reaction can be characterized by the measurement of MPL. In other words, the increase of SF reaction decreases the magnitude of PL in the tetracene film and vice versa.

Fig. 2(b) shows the MPL response of the tetracene film. The MPC response of the tetracene-based diodes as previously discussed in Fig. 1 is also plotted in Fig. 2(b) for the comparison. We observe the initially decreasing and then increasing magnitude of MPL response. The MPL exhibits a negative magnitude of −2.39% around 300 Oe and a positive magnitude of approximate 3.3% at 1000 Oe. Merrifield *et al.* [21] reported the field dependence of the SF rate to the fluorescence intensity in tetracene crystals. The model interprets that the increment of SF rate at low magnetic field decreases the magnitude of the fluorescence. Therefore, the negative MPL response as depicted in Fig. 2(b) is an indication of the increasing SF reaction by the applied magnetic field, which leads to the decreased singlet excitons or singlet excited states in the tetracene film. When the dissociation of $(PPs)_1$ mostly contributes to the generation of photocurrent in the tetracene-based diodes, the increasing SF reaction by the applied magnetic field would decrease the