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Modulations in line shapes of magnetoconductance curves for diodes of pentacene:fullerene charge transfer complexes

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ABSTRACT

This work investigates that the applied electric field modulates the line shapes of magnetoconductance (*MC*) responses in pentacene:fullerene diodes under illumination. We attribute the line shape of *MC* curves herein is correlated with the strength of the exchange interaction in pentacene:fullerene charge transfer (CT) complex states. Applying the reversed bias increases the built-in electric field ($E_{\text{built-in}}$) of the diodes to offset the exchange interaction of CT complex states and narrows the line shapes of *MC* responses. The saturation field of *MC* curves in the pentacene:fullerene bulk heterojunction device is 752 Oe when the device is biased at 0.4 V and decreases to 212 Oe at a reversed bias of −1.0 V. The line shape of *MC* curves for the diode made of pristine pentacene or fullerene as the active layer does not change with the applied bias voltage. Our results indicate the correlations of *MC* responses with the exchange interaction of CT complexes as modulated by the applied electric field.

Recently increased attention has focused on large magnetoconductance (*MC*) responses at room temperature in organic semiconductor devices with studies indicated that, in addition to device resistance and current, the applied magnetic field also has an impact on electroluminescence, photoluminescence photocurrent, capacitance, photo-induced absorption [1,2,5–7]. These diverse magnetic field effects (MFEs) indicate that organic semiconductors are suitable for application in spintronic and magneto-optoelectronic devices. The applications of MFEs include the development of the spin-polarized organic light-emitting diodes and the use of ferromagnetic thin films to induce the magnetic fringe fields for organic conjugated molecules [8,9]. Several models have been proposed to explain the mechanisms of MFEs [1,2,4,7,10,11]. Since the generation of MFEs in organic semiconductor devices usually correlates with excited states, the impact of the formation of excited states on MFEs is a major research issue [6,7,11–13].

Frankevich et al. proposed the intersystem crossing (ISC) of excited states with relatively long electron–hole (e–h) separation distance in conjugated molecules; that is, polaron pairs (PPs), can be changed by applying a magnetic field [1]. Since singlet and triplet states have different photo-physical properties, varying the relative populations between singlet and triplet states results in the MFEs in organic semiconductor devices [2,7,11]. In organic diodes

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using donor/acceptor (D/A) molecules as the active layer, the application of a magnetic field modulates the ISC of an intermolecular excited state, that is charge transfer (CT) complex state [7,12,13]. Since the e–h separation distance of CT complex states is relatively long (or the Columbic interaction is relatively weak) as compared to that of intramolecular excited states (excitons), the electric field, such as the applied bias voltage on the device or built-in electric field ($E_{\text{built-in}}$), possibly dissociates the CT complex states, reducing the influence of the applied magnetic field on the CT complex states and suppresses the device's MFEs [12,14]. Accordingly, we may expect that the e–h separation distance or Coloumbic interaction of CT complex states, along with the energy difference between singlet and triplet states (or exchange energy) are tunable by the electric field. Since line shapes of *MC* response depend on internal magnetic fields (or interactions) in organic semiconductors, the changes on $E_{\text{built-in}}$ would possibly modulate the line shapes of *MC* responses by varying the exchange interaction of CT complex states [3,15–18].

This study investigates the line shape narrowing of the *MC* response in pentacene:fullerene diodes under illumination. We assume that line shapes of *MC* responses are correlated with the e–h separation distance of CT complex states. Applying a reversed bias increases the $E_{\text{built-in}}$ of the diode as well as the e–h separation distance of CT complex states to offset the exchange interaction and narrows the line shape. By curve fitting, the saturation field of the *MC* response in a pentacene:fullerene bulk heterojunction device is 752 Oe at 0.4 V and decreases to 212 Oe at -1.0 V. On the other hand, the line shape of *MC* responses for a diode made by pristine pentacene or fullerene as active layer does not change with the applied bias voltage. These results highlight the correlation between the line shape of *MC* responses and the exchange interaction of CT complex states as modulated by the applied electric field.

Organic diodes were fabricated by sandwiching an active layer between a transparent electrode and a metal electrode. The transparent electrode comprised a clean indium-tin-oxide (ITO) covered glass substrate (RITEK Corp., 15 Ω/□) that was coated with poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS; Baytron P, Bayer AG, Germany) as a hole transport layer. Either pentacene:fullerene (1:0.5, 80 nm) (bulk heterojunction (BHJ) configuration) or pentacene (40 nm)/fullerene (40 nm) (planar heterojunction (PHJ) configuration) was thermally deposited on the substrate as an active layer under a vacuum ($\sim 3 \times 10^{-6}$ torr). The cathode was formed by depositing LiF (0.5 nm)/Al (100 nm) on top of the active layer. The blending ratio of fullerene to pentacene was determined by monitoring the deposition rates of the two sources during thermal co-evaporation. The active area of the device was 6 mm^2. All steps for the fabrication were performed in a nitrogen-filled glove box except for the preparation of the PEDOT:PSS layer. *MC* measurements were performed by mounting the device in a vacuum tube ($\sim 10^{-3}$ torr) between the poles of an electromagnet with the direction of current flowing perpendicular to the applied magnetic field. All measurements were made at room temperature, and the *MC* responses were found to be independent of the direction of the applied magnetic field. All *MC* measurements were made under illumination from a halogen lamp. The effect of drifting stress at constant bias were eliminated as described elsewhere [19]. Here, the *MC* ratio is defined as $MC = \triangle I(B)/I(0) = (I(B) - I(0))/I(0)$, where $I(B)$ and $I(0)$ are respectively the device current with and without an applied magnetic field.

Fig. 1(a) shows the *MC* responses in an ITO/PEDOT:PSS/pentacene:fullerene (1:0.5, 80 nm)/LiF/Al BHJ device at various bias voltages (0 – 0.4 V) under illumination. All the curves exhibit a positive *MC* response at 1000 Oe under various applied bias voltages, but the *MC* curves still contain a small and negative component in the low field regime (<100 Oe). Our previous studies had indicated that the positive *MC* response is correlated with the formation of the D/A interface in the device. Since CT complex states are formed in D/A interface, under applied magnetic field, the increased dissociation current from singlet CT complex

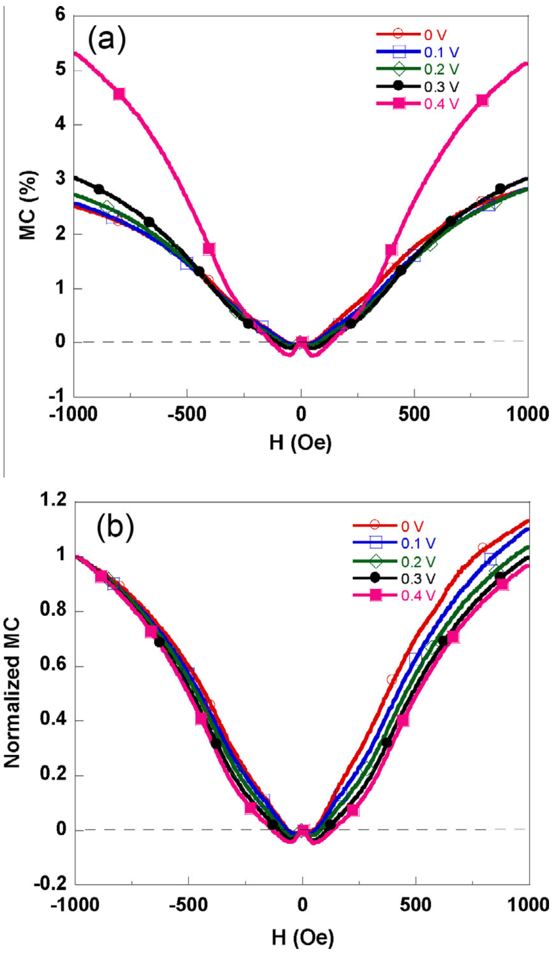

Fig. 1. (a) *MC* responses under illumination at various bias voltages in an ITO/PEDOT:PSS/pentacene:fullerene (1:0.5, 80 nm)/LiF/Al BHJ device. The applied bias voltages are (○) 0 V, (□) 0.1 V, (◇) 0.2 V, (●) 0.3 V, and (■) 0.4 V. (b) Normalized *MC* responses under illumination at various bias voltages in an ITO/PEDOT:PSS/pentacene:fullerene (1:0.5, 80 nm)/LiF/Al BHJ device. The applied bias voltages are (○) 0 V, (□) 0.1 V, (◇) 0.2 V, (●) 0.3 V, and (■) 0.4 V.