Modulating the line shape of magnetoconductance by varying the charge injection in polymer light-emitting diodes

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We fabricate the phenyl-substituted poly(p-phenylene vinylene) copolymer (super yellow, SY-PPV)-based polymer light-emitting diodes (PLEDs) with different device architectures to modulate the injection of opposite charge carriers and investigate the corresponding magnetoconductance (MC) responses. At the first glance, we find that all PLEDs exhibit the positive MC responses. By applying the mathematical analysis to fit the curves with two empirical equations of a non-Lorentzian and a Lorentzian function, we are able to extract the hidden negative MC component from the positive MC curve. We attribute the growth of the negative MC component to the reduced interaction of the triplet excitons with charges to generate the free charge carriers as modulated by the applied magnetic field, known as the triplet exciton-charge reaction, by analyzing MC responses for PLEDs of the charge-unbalanced and hole-blocking device configurations. The negative MC component causes the broadening of the line shape in MC curves. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5016882

I. INTRODUCTION

Organic spintronics, a research field that studies the electrical, optical and magnetic behaviors of advanced spintronic devices using organic semiconductor,1–3 has attracted much attention in the past few decades owing to its long spin lifetimes,4 ease of fabrication and preparation processes, and the low cost for the device fabrication.5 Organic magnetoconductance (MC) effect is one of the attractive uniqueness in organic spintronics research. Organic MC is the phenomenon where an external magnetic field can modulate the current of the device.6–9 This phenomenon has been widely used to study the magnetic field effect in many electronic devices such as photovoltaic cells, field effect transistors, and light-emitting diodes.10–13 There are several studies to find MC effect in polymer light-emitting diodes (PLEDs) using different kind of polymer materials. The current in the devices can increase or decrease with the applied magnetic field, which is known as the positive or negative MC responses, respectively. Hu et al. reported that MC responses of the devices using the same active layer material can be positive or negative, depending on balanced or unbalanced bipolar injection of charge carriers.14 Adjusting the electron and hole injection in the devices effectively reverses the positive MC to the negative MC response. Under different experimental conditions, MC responses exhibit the negative, positive, or both components (positive and negative) in the same materials.

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The sign of MC curves can be either positive or negative by varying the device structures, active materials, and experimental conditions, such as illumination, external bias voltage, and temperature. Hu et al. observed the negative MC response when the triplet exciton-charge reaction in the active layer dominates the generation of the current in a charge-unbalanced device, because of the reduced interaction between triplet excitons with the excess charges by an external magnetic field. Modulating the dissociation of the excited states (positive MC component) and triplet exciton-charge reaction (negative MC component) by the applied magnetic field, changes the sign of MC curves. Wang et al. investigated magnetic field effect of MC and magnetoelectroluminescence (MEL) for devices made of poly(p-phenylene vinylene) derivative, namely poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene), with [6,6]-phenyl C61-butyric acid methyl ester. The positive MC response is attributed to the change of the spin sublevels mixing via the hyperfine interaction in electrostatically bound electron-hole polaron pairs by the magnetic field and the negative MC component is caused by the change in spin mixing of electron and hole bipolarons. Bloom et al. demonstrated the change of MC sign from negative MC to positive MC response as the increase of applied bias voltage in poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-p-phenylene vinylene)-based PLED. They attributed the change of the sign for MC responses to the transition from unipolar to bipolar charge transport in the device. There are many experimental studies reported to interpret the inversion of MC responses from positive to negative and vice versa, but it should be noted that the negative MC component might hide behind the positive MC curves.

Here, we used the mathematical analysis to characterize the negative MC component that is possibly correlated with the triplet exciton-charge reaction. We design PLEDs based on a phenyl-substituted poly(p-phenylene vinylene) copolymer (super yellow, SY-PPV) with different injections of opposite charge carriers including the charge-balanced, charge-unbalanced, and hole-blocking injection and investigate the corresponding MC responses. At the first sight, all of our devices exhibit a positive MC response. Through fitting MC curve by a non-Lorentzian and a Lorentzian function, the negative MC component can be extracted from the positive MC response for PLEDs of the charge-unbalanced injection. We assume that the development of the negative MC component originally results from the decreased triplet exciton-charge reaction to generate the free charge carriers as modulated by the external magnetic field. The influence of the interaction of the triplet excitons with the excess charges to contribute to the MC response by the applied magnetic field is further enhanced in PLEDs of hole-blocking device configuration. Accordingly, the results suggest that the increasing negative MC component broadens the line shape of MC curves, in which the modulation of triplet exciton-charge reaction within SY-PPV layer in PLEDs can be characterized by analyzing MC responses for devices of the balanced, unbalanced, and hole-blocking injection of charge carriers.

II. EXPERIMENTAL TECHNIQUE

Indium-tin-oxide (ITO)-coated glass with a sheet resistance of 15 Ω/square was used as the substrate (RITEK Corp.). The routine cleaning processes comprise of sonication in detergent, rinsing in de-ionized water, and the final UV ozone treatment. A hole transport layer, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS, Baytron P, Bayer AG, Germany) was spin-coated at a speed of 4000 rpm on the patterned glass/ITO substrate. The glass/ITO/PEDOT:PSS substrate was annealed at 150 °C for 25 min to remove the residue of water molecules. The SY-PPV (PDY-132 Merck, 0.5 wt% in toluene) was spin coated at a speed of 2000 rpm. The bathocuproine (BCP, Aldrich) (10 nm), LiF (1 nm), and Al (100 nm) were deposited by a vacuum thermal evaporator on SY-PPV layer at a pressure of 6x10^-6 torr. Except for the preparation of PEDOT:PSS layer, all fabrication processes were done inside the nitrogen-filled glove box with both moisture and oxygen levels below 1 ppm. The area of our devices is 6 mm². We fabricated three kinds of devices to investigate the MC responses of SY-PPV-based PLEDs with different device architectures. Figure 1(a)–(c) show the schematic diagram of energy levels for the device configurations used in this paper. The devices consist of (a) glass/ITO/PEDOT:PSS/SY-PPV/LiF/Al (charge-balanced device), (b) glass/ITO/PEDOT:PSS/SY-PPV/Al (charge-unbalanced device), and (c) glass/ITO/PEDOT:PSS/SY-PPV/BCP/Al (hole-blocking device).
FIG. 1. The schematic diagram of energy levels for the device configurations used in this paper. The devices consist of (a) glass/ITO/PEDOT:PSS/SY-PPV/LiF/Al (charge-balanced device), (b) glass/ITO/PEDOT:PSS/SY-PPV/Al (charge-unbalanced device), and (c) glass/ITO/PEDOT:PSS/SY-PPV/BCP/Al (hole-blocking device). HOMO and LUMO represent the highest occupied molecular orbital and lowest unoccupied molecular orbital of the conjugated molecules, respectively.

The $J-V$ (current density – voltage) characteristics of SY-PPV-based PLEDs were measured using a source meter (Keithley 2400). MC measurements were performed at room temperature by mounting the devices in a vacuum tube ($\sim 10^{-3}$ torr) between the poles of an electromagnet in perpendicular direction to the current direction. The MC curves were averaged to eliminate the influence of drifting at different biases. $^{11,20}$ MC magnitude is defined as: $MC = \Delta I(B)/I(0) = (I(B) - I(0))/I(0)$, where $I(B)$ and $I(0)$ are respectively the device current with and without an applied magnetic field. The interval for the change of the magnetic field in MC measurement is 20 Oe. There are totally 100 data points between -1000 and 1000 Oe in our measurement.

III. RESULTS AND DISCUSSION

Figure 2(a) and (b) shows the plot of MC responses for the charge-balanced and charge-unbalanced SY-PPV-based PLEDs, respectively, at various applied bias voltages (from 3 to 7 V). The
positive MC responses as depicted in Figs. 2(a) and (b) are associated with the dissociation of electron-hole pairs\textsuperscript{21} that do not recombine, reducing the recombination current and by this way increasing the number of charges that cross the device. Therefore, the balanced injection of charge carriers supports the efficient generation of electron-hole pairs and results in the higher magnitude of the positive MC response as presented in Fig. 2(a). The charge-balanced SY-PPV-based PLED also exhibits a positive MEL response under various applied bias voltages as depicted in Figure S1 in supplementary material. However, the applied electric bias would facilitate the dissociation of electron-hole pairs and reduce the influence of applied magnetic field on the excited states. We observed the decreased positive MC response for both charge-balanced and charge-unbalanced devices with increasing the bias voltages (3 to 7 V) as shown in Figs. 2(a) and (b). The above observations agree well with the proposed model that the dissociation of electron-hole pairs under the applied magnetic field contributes to the positive MC response.\textsuperscript{22}

In order to examine the underlying mechanisms of MC responses in SY-PPV-based PLEDs, we performed the curve fitting by applying a combination of two empirical equations of a non-Lorentzian and Lorentzian function as shown in the equation below:\textsuperscript{13,16,23}

\[
MC = A_{01} \frac{B^2}{(|B| + B_{01})^2} + A_{02} \frac{B^2}{B^2 + B_{02}^2}
\]  

(1)
Where $A_{01}$ and $A_{02}$ are pre-factors, $B_{01}$ and $B_{02}$ are the saturation fields for the non-Lorentzian and Lorentzian function, respectively, and $B$ is the applied magnetic field. The positive and the negative MC component are extracted from the curve fitting of MC response, the non-Lorentzian function and the Lorentzian function in Eq. 1, respectively. According to the fitting results, as depicted in Fig. 3(a), the MC response can be fitted by the positive component (the non-Lorentzian function in Eq. 1). The negative component (the Lorentzian function in Eq. 1) in the charge-balanced SY-PPV-based device is independent with the applied magnetic field and negligible. On the other hand, we observe an appreciable negative MC component in MC curves of the charge-unbalanced device as illustrated in Figure 3(b). As depicted in Fig. 1(b), the schematic diagram of energy levels for the charge-unbalanced device, the injection of electron from Al cathode into SY-PPV active layer would be difficult due to the large injection barrier height. Accordingly, holes would be the dominant carriers in the charge-unbalanced device. We reasonably assume that the formation of the negative MC component is related to the excess carriers (holes) in charge-unbalanced SY-PPV-based PLED.

The processes of the triplet exciton-charge reaction involved in the generation of free charge carriers from the interaction between triplet excitons with excess charges in SY-PPV-based PLEDs. In other words, the excess charge carriers in SY-PPV active layer react with triplet excitons to contribute to the current. Since the triplet exciton-charge reaction is a magnetic field sensitive process, the

![Graph](image_url)

FIG. 3. The fitting results (at 4 V) for the (a) charge-balanced (b) charge-unbalanced device.
applied magnetic field decreases the interaction of the excess charges with triplet excitons in charge-unbalanced SY-PPV PLED and yields the negative MC component. This assumption can be verified by further increasing the concentration of excess carriers (holes) in SY-PPV active layer and examining MC responses of hole-blocking SY-PPV PLEDs.

Figure 4(a) shows the plot of the MC responses for the hole-blocking SY-PPV-based PLEDs at various applied bias voltages (from 3 to 7 V). The observations about the positive MC responses and decreased MC magnitudes with increasing bias voltages agree with the previous discussion related to Figs. 2(a) and (b). Figure 4(b) presents the fitting results of the hole-blocking SY-PPV-based PLED by Eq. 1. It is to be noted that the magnitude of the negative MC component for the hole-blocking SY-PPV-based PLED as shown in Fig. 4(b) is more evident than that of the charge-unbalanced devices in Fig. 3(b). As depicted in Fig. 1, the schematic diagram of energy levels for the hole-blocking device, the deep highest occupied molecular orbital (-6.5 eV) of BCP layer blocks the transport of holes to reach the electrode as well as to increases the concentration of holes in SY-PPV layer. The excess carriers further increase the triplet exciton-charge reaction in the hole-blocking device to dominate MC responses than that of the charge-unbalanced device. Accordingly, the applied magnetic field shows the higher influence on the triplet exciton-charge reaction to increase the magnitude of the negative MC component in the hole-blocking SY-PPV-based PLED as shown in Fig. 4(b). The result fortifies

**FIG. 4.** (a) MC responses for the hole-blocking SY-PPV-based PLEDs at various applied bias voltages (from 3 to 7 V). (b) The fitting results (at 4 V) for the hole-blocking device.
our assumption that the negative MC component of MC responses in our study is associated with the triplet exciton-charge reaction, a magnetic field-sensitive process. Figure 5(a) depicts the normalized MC responses for the charge-balanced, charge-unbalanced, and hole-blocking devices. Although MC responses are all positive in these devices, the line shape of MC curves for the charge-unbalanced and hole-blocking SY-PPV-based PLEDs changes compared to that of charge-balanced device due to the negative component as seen in Fig. 3(b) and Fig. 4(b). Apparently, the high magnitude of the negative component in hole-blocking device broadens the line shape of MC responses. As shown in Fig. 5(a), the line shape of the hole-blocking SY-PPV-based PLEDs is wider than that of the charge-unbalanced and charge-balanced device.

It is also found that line shape of MC responses changes with the applied electric bias. Figure 5(b) depicts the ratios of the pre-factors, \( \frac{A_{02}}{A_{01}} \), of the non-Lorentzian and Lorentzian function in Eq. 1 to fit MC responses of the charge-balanced, charge-unbalanced, and hole-blocking devices versus the electric bias. The \( \frac{A_{02}}{A_{01}} \) ratios also represent the proportions of the negative to positive MC component in MC curves. In Fig. 5(b), the magnitude of \( \frac{A_{02}}{A_{01}} \) is relatively higher (in the negative magnitude) in the hole-blocking device than that of the charge-unbalanced and charge-balanced device. The results clearly indicate that the magnitude of the negative component is correlated with the

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**FIG. 5.** (a) The normalized MC responses for the charge-balanced, charge-unbalanced, and hole-blocking devices. (b) The ratios of the pre-factors, \( \frac{A_{02}}{A_{01}} \) to fit MC responses of the charge-balanced, charge-unbalanced, and hole-blocking devices versus the electric bias.
triplet exciton-charge reaction in SY-PPV active layer for the charge-unbalanced and hole-blocking devices. Additionally, applying the high electric bias on the device would enhance the injection of electrons from Al cathode into SY-PPV active layer to balance the concentration of opposite charge carriers. As a result, the magnitude of $A_{02}/A_{01}$ ratios in the charge-unbalanced and hole-blocking devices decrease with increasing the electric bias, because of the reduced triplet exciton-charge reaction in the charge-balanced regime. As shown in Fig. 5(b), the $A_{02}/A_{01}$ magnitude as extracted from the charge-balanced SY-PPV-based PLED is relative low (negligible negative MC component). The applied electric bias has only little effect to modulate $A_{02}/A_{01}$ magnitude and the line shape of MC response for the charge-balanced device.

Lei et al.\textsuperscript{24} also reported that a positive MC curve is composed of the positive MC and negative MC component at the low and high magnetic field, respectively, in tris-(8-hydroxyquinoline) aluminum-based device. They proposed that the positive MC component at the low field is associated with the hyperfine mixing between singlet and triplet electron-hole pairs, and the negative MC component at the high field is induced by the charge reaction of triplet excitons. Their investigation agrees well with our observations that the negative MC component raises from the triplet exciton-charge reaction. In addition, our results basically agree with previous works that the negative component in MC responses is correlated with the interaction between triplet excitons with charges.\textsuperscript{9,14,25} In this study, the design of the hole-blocking device further enhances the triplet exciton-charge reaction, thereby modulating the line shape of MC responses.

IV. CONCLUSION

In conclusion, we had applied the mathematical analysis based on the curve fitting of a non-Lorentzian and a Lorentzian function to investigate MC responses of SY-PPV-based PLEDs of charge-balanced, charge-unbalanced, and hole-blocking device configurations. We are able to identify a negative MC component in positive MC curves of the charge-unbalanced device. The negative MC component is further enhanced in the device of the hole-blocking configuration. We attribute the development of the negative MC component to the decreased interaction of the triplet exciton-charge reaction to generate the current as modulated by the applied magnetic field. As a result, the negative MC component modulates the line shape of MC responses and broadens MC curves in charge-unbalanced and hole-blocking devices. Our results reveal the hidden negative MC component and its correlations with the triplet-excitons charge reaction to modulate MC responses.

SUPPLEMENTARY MATERIAL

See supplementary material for the MEL response of the charge-balanced SY-PPV-based PLED.

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