Organic Electronics 14 (2013) 1376–1382

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Antagonistic responses between magnetoconductance and magnetoelectroluminescence in polymer light-emitting diodes

Kai-Wei Tsai [a], Tsung-Hsun Lee [b,c], Jin-Han Wu [a], Jing-Yuan Jhou [a], Wei-Shun Huang [b], Sung-Nien Hsieh [a], Ten-Chin Wen [a,d,*], Tzung-Fang Guo [b,d,*], J.C.A. Huang [c,d,*]

[a] Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan
[b] Institute of Electro-Optical Science and Engineering, National Cheng Kung University, Tainan, Taiwan
[c] Department of Physics, National Cheng Kung University, Tainan, Taiwan
[d] Advanced Optoelectronic Technology Center, National Cheng Kung University, 70101 Tainan, Taiwan

ARTICLE INFO

Article history:
Received 29 June 2012
Received in revised form 18 January 2013
Accepted 23 February 2013
Available online 20 March 2013

Keywords:
Interfacial layer
Magnetoconductance
Magnetoelectroluminescence
Polymer light-emitting diodes

ABSTRACT

Antagonistic responses between magnetoconductance (MC) and magnetoelectroluminescence (MEL) in the polymer light-emitting diodes with an interfacial layer between Al cathode and active layer are simultaneously measured. As the interfacial layer (tetraoctylammonium bromide) is used, the significant increase in the number of injected negative polarons and the blocking of positive polarons promote the triplets-(free polaron) reaction and provide a good explanation for the reason that electroluminescence (EL) efficiency is maximal in the trap free space charge limited current regime at high bias. By fitting of MC and MEL curves using Lorentzian and non-Lorentzian empirical equations, three magnetic field dependent mechanisms, which are the intersystem crossing between singlet/triplet polaron pairs, the triplets-(free polaron) reaction, and the triplets-(trapped polaron) reaction are elucidated. The distribution of the three components is tunable by varying the applied electric field, which primarily modulates the triplets-(free polaron) reaction rate. The results pave a new route toward understanding the mechanism of organic spintronics for developing of multifunctional devices.

1. Introduction

In recent years, advanced spintronic devices have been fabricated using organic semiconductors, which exhibit interesting electrical, optical and magnetic responses [1–4]. This emerging field of research is called organic spintronics. One of the important issues in organic spintronics field is organic magnetoconductance (MC) which is the study of electrical response due to magnetic field in organic electronic devices such as light emitting diodes, photovoltaic cells, and field effect transistors [5–8]. Applying a magnetic field to such devices can remarkably affect their conductivity and electroluminescence [9,10]. Study of the characteristics of magnetic field effect is essential not only for understanding the underlying mechanisms in organic MC but also for developing novel devices [11,12].

The mechanism by which a magnetic field effect on organic semiconductor is often determined by the formation of spin-dependent excited states, including excitons and polaron pairs (PPs) [5–10,13,14]. Applied magnetic field can modify the distribution of both singlet and triplet excited states and can change the polaron reaction rates of excitons [6,10,11,13,15,16]. Additionally, the magnetic field effects of excited states depend on whether the carrier injection is balanced or not, which can be controlled by modifying the interfacial electronic structure and the applied electric field.

The interfacial layer between electrode and active layer can be used to manipulate the electronic structure of inter-

* Corresponding authors. Address: Advanced Optoelectronic Technology Center, National Cheng Kung University, 70101 Tainan, Taiwan.
E-mail addresses: tcwen@mail.ncku.edu.tw (T.-C. Wen), guotf@mail.ncku.edu.tw (T.-F. Guo), jcahuang@mail.ncku.edu.tw (J.C.A. Huang).

1566-1199/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.orgel.2013.02.031

face, which is crucial for the exciton-formation efficiency or the capacity of carrier injection and collection in organic devices. The tunable interfacial characteristics have made a great impact on studies of magnetic field effect in organic electronics [11,17]. Most organic MC studies are centered on magnetic field effect of the bulk contribution in organic semiconductors but ignore how the interfacial structures affect carrier injection and collection [1,18]. To prevent damage by the diffusion of metal into the polymer active layer and to improve carrier injection, the use of an electrode buffer layer before deposition of the metal cathode is a favorable option for polymer devices. Various buffer layers, such as ionic salt, ionic polymer or metal–oxide have been adopted to modify polymer devices [19–21]. Recent studies have proposed that ionic salt not only serves as a buffer layer to protect the polymer active layer from damage during metal deposition but also creates interfacial dipole to promote carrier injection and collection [20,21]. Therefore, the use of ionic salt as cathode buffer can significantly improve the electroluminescent efficiency (EL efficiency) of organic devices. For example, tetraoctylammonium bromide (TOAB) is very effective as electron injection layer for cathode-independent high-efficiency polymer light-emitting diodes (PLEDs) [22].

In this work, we report the magnetic field effect on PLEDs without ferromagnetic electrodes, Indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)/green poly(9,9-dialkylfluorene) derivative (G-PF)/TOAB/Al (TOAB/Al-device), that yields surprising results of antagonistic responses between MC and magnetoelectroluminescence (MEL), which has never been studied to our knowledge. We identify that the antagonistic magnetic responses in TOAB/Al-device can be understood as involving three magnetic mechanisms, the magnetic field-dependent intersystem crossing between singlet/triplet polaron pairs [11,16], the triplets-(free polaron) reaction [10,24–26], and the triplets-trapped polaron reaction [3,11,24,25,27]. Moreover, the applying biases can modify the relative contribution of these three components to MC and MEL responses, suggesting that the three mechanisms are correlated with the ability of carrier injection and the applied electric field. In particular, the predominant effect due to triplets-(free polaron) reaction can increase electroluminescence (EL) efficiency and can be tuned by the applied magnetic field.

2. Experimental

Devices were fabricated by spin-coating G-PF (EL emission centered at 560 nm) from 1 wt% toluene solution onto ITO-coated glass substrates that were wet cleaned, UV/O_3 treated, and then covered with PEDOT: PSS (Bayer Corp. 4083). After 6000 rpm for 60 s spin cast on the top of PEDOT: PSS, the G-PF film was baked at 65 °C for 30 min. TOAB was purchased from Fluka. Co. The TOAB solution was prepared from 0.2 wt% 2-methoxyethanol and stirred 12 h prior to use. A solution containing the ionic salt was spin-coated onto the surface of G-PF at 8000 rpm for 60 s and then the film was baked at 100 °C for 10 min. Devices were completed by thermal evaporation of the metal cathode at a pressure of 10^{-6} hPa. All procedures, except the casting of the PEDOT: PSS layer, were performed in a N_2-filled glove box.

The current–voltage–luminance (J–V–L) measurements were performed using a Keithley 2400 source measure unit and a Keithley 2000 digital multimeter with a silicon photodiode (Hamamatsu S2387), and calibrated using a Photoresearch PR650 spectrometer.

As for magnetic field measurements including MC and MEL, the devices were placed in the current direction perpendicular to the direction of magnetic field, and were mounted in the middle of a vacuum tube (vacuum condition $\sim 7.0 \times 10^{-3}$ hPa) which was placed between the two magnet poles. The curves of magnetic field measurements were averaged to eliminate the influence of drifting at different biases [7,23]. The MC and MEL magnitudes are defined as:

$$\mathrm{MC} = \frac{\Delta I(B)}{I(0)} = \frac{I(B) - I(0)}{I(0)}, \quad \mathrm{MEL} = \frac{\Delta \mathrm{EL}(B)}{\mathrm{EL}(0)} = \frac{\mathrm{EL}(B) - \mathrm{EL}(0)}{\mathrm{EL}(0)}$$

$I(B)$ is the current of the devices with the applied magnetic field. $\mathrm{EL}(B)$ is the magnetic field dependent electrical emitting intensity of the devices. All the magnetic field measurements were performed at room temperature.

3. Results and discussion

3.1. The J–V–L behaviors of PLED devices

In order to study magnetic field effect of PLED, two PLEDs were fabricated as TOAB/Al-device and Ca/Al-device. Fig. 1a plots the J–L–V curves for these two devices. For the sake of comparison, the detailed data of device performances are tabulated in Table 1. At a bias voltage of 7.0 V, TOAB/Al-device and Ca/Al-device show current density 462.5 and 887.9 mA/cm^2 as well as light intensity 34,659 and 43,915 cd/m^2, respectively. The similar current turn-on voltage and light turn-on voltage in TOAB/Al-device and Ca/Al-device suggest that the built-in potential and the negative polaron injection barrier are similar in both devices. At a current of 5 mA, the EL efficiency of TOAB/Al-device and Ca/Al-device are 10.26 and 7.18 cd/A, respectively. The lower current density (J) and the similar light intensity of TOAB/Al-device at bias of 7 V are attributable to the blocking of positive polaron in the interface between G-PF and Al, resulting in more exciton formation. Fig. 1b plots both EL efficiency and J as functions of the applied bias in TOAB/Al-device and reveals injection, transportation, and recombination behavior of polarons. According to the full-logarithm J–V curve, the maximum of EL efficiency in TOAB/Al-device is located at higher bias apart from the starting point of trap free space charge limited current (SCLC) region [24,25]. This result indicates that TOAB/Al cathode injects more negative polaron at high bias to achieve the balanced injection. According to the J–L–V characteristic of TOAB/Al-device, the blocking of positive polaron and the more negative polaron injection are proposed to increase the probability of interaction between the triplet exciton and the injected negative polaron. This