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Modulating the competition between dissociation and spin mixing in electron–hole pairs: An investigation of ultra-small field induced magnetoconductance responses in blended devices

Qiaoming Zhang [a], Yanlian Lei [a], Weiyao Jia [a], Lijia Chen [a], Yong Zhang [a], Xiaohui Yang [a], Yintao You [b], Zuhong Xiong [a,*]

[a] School of Physical Science and Technology, MOE Key Laboratory on Luminescence and Real-Time Analysis, Southwest University, Chongqing 400715, PR China
[b] State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Shanghai 200433, PR China

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ABSTRACT

The ultra-small field induced magnetoconductance (MC) responses in Supper Yellow Poly(phenylenevinylene) (SY-PPV):Phenyl-C61-butyric acid methyl ester (PCBM) blends have been investigated to clarify the role of competition ratio by changing the dissociation rate. It is found that the widths of the ultra-small field induced MC curves broaden from 0.4 mT (0 wt.%) to 1.9 mT (4 wt.%). The characteristics of electroluminescence-voltage suggest that the width broaden is assigned to an increase in the competition ratio induced by an increase in the dissociation rate when PCBM is blended. This conclusion is further verified by an empirical formula fitting.

1. Introduction

Organic magnetoconductance (MC) defined as the relative change of electrical conductance with and without an external magnetic field, has fuelled up much attention due to their theoretical values and potential applications [1–19]. In order to reveal the origin of the MC effect, several mechanisms have been proposed, mainly including bipolaron mechanism [1], electron–hole (e–h) pair mechanism [2–5] and triplet–polaron interaction mechanism [6–8] in the literatures. It is noteworthy that the three above mechanisms contain a common process [9–14], the hyperfine-induced spin mixing within polaron pairs (bipolaron pairs and e–h pairs). Therefore, much attention has been paid to reveal the spin mixing process [9–14].

In general, two important parameters, the hyperfine coupling constant (a_{HF}) and the competition ratio (r), should be considered in spin mixing process for the MC response. The first parameter, a_{HF}, has been certified by Nguyen et al. [9,10] through comparing the MC responses in the hydrogenated and deuterated polymers at low magnetic field. An additional structure in the MC response following "sign-reversal" phenomenon has been found around 1–2 mT-range in their work. This type of MC is called ultra-small field induced MC effect, which is usually considered closely to the hyperfine-induced spin mixing. The second parameter, competition ratio r ($r = q/\omega_{hf}$), be defined as the ratio between dissociation rate (q) and the typical hyperfine precession frequency (ω_{hf}), is still not very clear. Some theoretical work [11–14] has demonstrated that the MC response could be affected by modulating the competition through changing the dissociation rate of e–h pairs if the ω_{hf} keeps unchanged. However, there is

* Corresponding author.
E-mail address: zhxiong@swu.edu.cn (Z. Xiong).

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still no direct experimental study for the effect of competition ratio on the MC response.

To modify the competition ratio, Phenyl-C61-butyric acid methyl ester (PCBM), which is usually utilized in organic photovoltaic (OPVs), is an ideal candidate. This is because the dissociation rate could be increased when PCBM is blended into host material with a low concentration. Moreover, in order to unravel the role of competition in the spin mixing process, much attention should be paid on the utral-small field induced MC effect, in which much perturbation has been removed [12].

In this letter, we investigate the ultra-small field induced MC effect in the Supper-Yellow Poly(phenylenevinylene) (SY-PPV):PCBM blends to provide an experiment study for the role of the competition between dissociation and spin mixing on the MC response by changing the PCBM concentration. The MC responses in all blends show "sign-reversal" phenomenon, symmetrically containing a negative component firstly and then a positive component, exhibiting a "W" line shape. However, the widths of the ultra-small field induced MC curves broaden from 0.4 mT (0 wt.%) to 1.9 mT (4 wt.%). Electroluminescence (EL)-voltage characteristics curves indicate that the dissociation rate increases with enhancing the PCBM concentrations. And then, we suggest that the broadening in the curve width is assigned to the increasing of competition ratio which is caused by enhancing the dissociation rate of e–h pairs. The interpretation is verified quantitatively by an empirical formula fitting.

2. Experimental

The PCBM molecules were mixed into the SY-PPV by different weight ratios up to 4 wt.% in chloroform, forming PCBM doped polymer blend solutions. A 50 nm thick film of poly[3,4-ethyl-enedioxythiophene] poly[styrene sulfonate] (PEDOT:PSS) and 80 nm thick film of SY-PPV:PCBM blends were spin cast on pre-cleaned indium tin oxide (ITO) glass substrates, successively. The spin-cast films were then baked in a vacuum oven at 120 °C for 30 min. Therefore, the blend devices were fabricated with the architecture of ITO/PEDOT:PSS/SY-PPV:PCBM (c wt.%)/Calcium (Ca, 10 nm)/Aluminum (Al, 120 nm), by thermally evaporating Ca and Al electrode under vacuum pressure of 10^{-4} Pa through a shadow mask with active area of 1×2 mm^2. After fabrication, the devices were mounted on the cold finger in a close-cycle cryostat system (Janis CCS-350s) which was located between the pole pieces of an electromagnet (Lakeshore EM647) for the EL and MC measurements as described previously [20].

3. Results and discussion

Fig. 1 shows the MC response in the SY-PPV:PCBM blends (4 wt.%) and pristine SY-PPV in a low magnetic field region ($|B| < 8$ mT) at room temperature. The MC was defined as the relative change in current as a function of external B-field, i.e. $\mathrm{MC} = \Delta I/I = [I(B) - I(0)]/I(0)$. For the 4 wt.% blends [see in panel (a)], it is found that the MC symmetrical decreases firstly, and then turns to increase

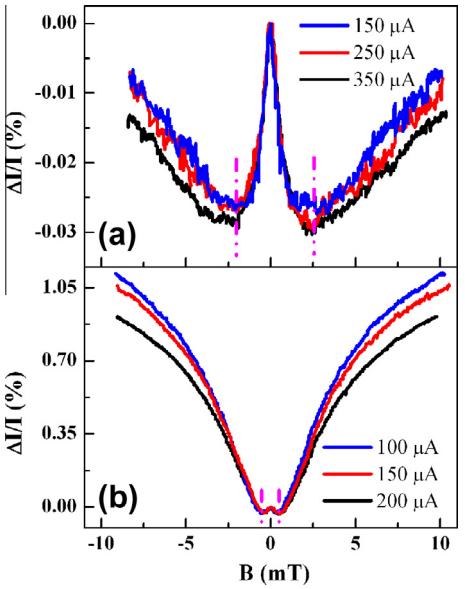

Fig. 1. The MC response ($\Delta I/I$) in 4 wt.% blend device (a) and pristine SY-PPV device (b) in a low magnetic field region ($|B| < 8$ mT) at room temperature.

slowly with enlarging the external B-field, showing "sign-reversal" phenomenon. The position of the "dip" (the minimum value of MC), which demarcates the width of the ultra-small field induced MC effect, is found to be located at ±1.9 mT and be independent on the applied bias voltages. For the pristine SY-PPV device [panel (b)], a tiny "sign-reversal" phenomenon is also observed in the MC response with a much smaller position at $B_m = \pm 0.4$ mT. Moreover, the magnitude of the MC values in the 4 wt.% blend devices is nearly 2 orders of magnitude lower than that in the pristine devices.

The "sign-reversal" phenomenon in MC response has already been observed in many other devices. In a recent study [21], we found a similar "sign-reversal" phenomenon in NPB-based device under laser illumination and suggested that the negative component could be attributed to the bipolaron formation. However, the position of the "sign-reversal" in that work is located at ±100 mT, which is much larger than the B_m value in these blend devices. In addition, Nguyen et al. [9,10] also found a "sign-reversal" phenomenon at such small B-field in a DOO-PPV-based device. They suggested that the ultra-small field induced MC effect was caused by the interplay of hyperfine and Zeeman interactions in polaron pairs.

In fact, the "sign-reversal" phenomenon of the MC response could be possibly understood according to the change in carriers' average precession frequency. In the absence of external B field, the spin of electrons and holes in e–h pairs processes around the random hyperfine fields (B_{hf}) from the nearby hydrogen nuclei. Thus, the inter-conversation between singlet and triplet e–h pairs could occur due to the different precession frequency and precession direction for spin between holes and electrons [11,15]. When an ultra-small external B field is applied, the effective magnetic field (B_{eff}) is a sum of the external B field