Magnetic Field Effects in π-Conjugated Polymer-Fullerene Blends: Evidence for Multiple Components

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We studied magnetoconductance (MC) and magnetoelectroluminescence (MEL) in organic diodes from blends of π-conjugated polymers and fullerenes at various concentrations, c. The MC response is composed of several components that depend on the applied bias voltage and c. A dominant positive low-field (LF) component, which also governs the MEL response, dramatically decreases and broadens in the blends, thus unraveling a positive high-field and negative LF components. The positive MC components are caused by electrostatically bound e-h polaron pairs in unblended devices, and charge transfer pairs in the blends, which are dominated by two different field-induced spin sublevel mixing mechanisms. In contrast, the negative LF response is due to e-e and h-h pairs; this is confirmed by studying MC in electron- and hole-unipolar devices, which lack positive MC response.

Sizable organic magnetoresistance (OMAR) has been recently observed in a variety of light emitting diodes of π-conjugated polymers and small molecules with non-magnetic electrodes [1–10]. In fact OMAR has been studied for several years in the past [11,12]; however renewed interest has recently increased due to the high OMAR value obtained at room temperature (up to ~10%) induced by relatively small magnetic field of ~50 mT [1]. OMAR is the highest known magnetoresistance response in the class of semiconductor materials, and therefore has the potential to be used in magnetically controlled opto-electronic devices and magnetic sensors. It is thus one of the most unusual phenomena of "plastic" electronics, more specific "organic spintronics" [13], which makes this field attractive for both basic research and applications.

In spite of the latest surge of interest in OMAR; its underlying mechanism is still hotly debated. Because of the weak magnetic field involved, it is largely believed that OMAR originates from spin sublevel mixing via the hyperfine interaction (HFI) [1–12] (but see [14]), which is relatively small in π-conjugated organic semiconductors [12]. However, two competing basic models based on HFI have been proposed for explaining the spin-mixing process that causes OMAR. These are the excitonic model, in which the magnetic field modulates the singlet to triplet interconversion rate [3], or triplet-exciton polaron quenching [4], and the bipolaron model [6]. The exciton model is based on the spin dependent electrostatically bound polaron pairs (P^+P^-) formed from the oppositely injected P^+- and P^--currents in the device [3]; whereas the bipolaron model relies on the spin dependent formation of *doubly charged* excitations [6]. Therefore the exciton model is based on the existence of both P^+ and P^- in the device active layer; whereas the bipolaron model is viable also when only one type of charge carrier is injected into the device. OMAR has been shown to be positive or

negative depending on the applied bias voltage, V and temperature, [1,7,9], can be tuned between positive and negative values by changing the device architecture [8]; and is enhanced by device conditioning at high current densities [10].

In recent years the field of organic photovoltaic (OPV) has also dramatically advanced; and power conversion efficiency of organic solar cells approaching 6% has been reached in bulk heterojunction-type devices made of polymer-fullerene blends [15]. The polymer and fullerene constituents in such blends were shown to form *separate phases*, in which the photogenerated P^+ and P^- move rather independently from each other in the polymer and fullerene phase, respectively, for reaching the opposite electrodes [16]. In agreement with this ansatz, the bimolecular recombination kinetics in the blends was shown to be much weaker than in polymer films [16]. It is thus tempting to study OMAR in OPV devices made of polymer-fullerene blends, because the formation of PP species in such devices would be suppressed due to the phase separation; and this might unravel the correct OMAR underlying mechanism.

In this work we studied two magnetic field effects (MFE), namely, magnetoconductance (MC) and magneto-electroluminescence (MEL) in OPV devices made of blends of poly(phenylene-vinylene) (PPV) derivatives and fullerene molecules with various concentration, c, ranging from $c = 0$, to 50% (optimum blending), to 100% in weight. The obtained MC response at various c and V unravels the existence of several MC components. These are: (i) a dominant positive narrow low-field (LF) component that also determines the MEL response, which is due to HFI; (ii) a positive broad high-field (HF) component that is due to a different spin-mixing mechanism that is dominant for PP's in the blend devices, namely, "Δg mechanism" (see below); and (iii) a negative LF compo-

nent. The positive LF component dramatically decreases and broadens in the blends, and this favors the spin-mixing of PP's in the exciton model as its underlying mechanism; indeed this MC component lacks in unipolar devices at $c = 0$. In contrast, the negative LF component survives in bipolar OPV devices with $c = 50\%$ as well as in $c = 0$ electron- and hole-unipolar devices; and therefore it agrees with the bipolaron model.

The devices used for the MC measurements were 5 mm² diodes made from blend of PPV derivative, namely 2-methoxy-5-(2′-ethylhexyloxy) (MEH-PPV), with 1-(3-methoxycarbonyl) propyl-1-phenyl-[6,6]-methanofullerene (PCBM) at various concentrations, c ranging from $c = 0$ (unblended MEH-PPV) to $c = 50\%$ (optimal blending) to $c = 0$ (unblended PCBM), which was sandwiched between a hole transport layer: poly(3,4-ethylenedioxythiophene) (PEDOT)-poly(styrene sulphonate) (PSS), and capped with a transparent anode: indium tin oxide (ITO), and a cathode: calcium (protected by aluminum film). The unblended $c = 0$ (or $c = 100\%$) device was in the form of ITO/PEDOT:PSS/MEH-PPV (or PCBM)/Ca/Al. The $c = 0$ hole-unipolar device was ITO/PEDOT-PSS/MEH-PPV/Au, whereas the electron-unipolar device was Al/MEH-PPV/Ca/Al [17]. These devices did not show any measurable electroluminescence (EL), whereas the blended devices showed very little EL. The devices were transferred to an optical cryostat with variable temperature that was placed in between the pole pieces of an electromagnet producing magnetic field, B up to 300 mT. The devices were driven at constant V using a Keithley 236 apparatus; and the current, I and EL were simultaneously measured while sweeping B. For comparing the field-induced current change, ΔI (MC) and induced EL change, ΔEL (MEL), we simultaneously measured $\Delta I/I$ and $\Delta EL/EL$, which are defined as follow [1]:

$$\Delta I/I = \frac{I(B) - I(B = 0)}{I(B = 0)},$$
$$\Delta EL/EL = \frac{EL(B) - EL(B = 0)}{EL(B = 0)}.$$
(1)

With this definition MC > 0 (MEL > 0) when $\Delta I > 0$ ($\Delta EL > 0$).

Figure 1 shows the room temperature MC response in MEH-PPV/PCBM diodes at various PCBM concentrations ranging from $c = 0$ to $c = 100\%$. Several observations are noteworthy: (i) The positive MC response decreases by ∼ 2 orders of magnitude in the blends, changing from few percent at $c = 0$ to ~0.1% at $c = 50\%$; at the same time it also substantially broadens. (ii) The MC response changes with c and V. At $c = 0$ [panel (a)] MC changes sign from negative to positive at large V [7]; this is more pronounced for $c = 50\%$ [panel (c)]. (iii) The MC response broadens at large V; in fact the positive LF MC component decreases even at $c = 0$, and a *much broader* MC component, namely, a HF component is unraveled. This is more pronounced for $c = 10\%$ [panel (b)]. The LF MC response in
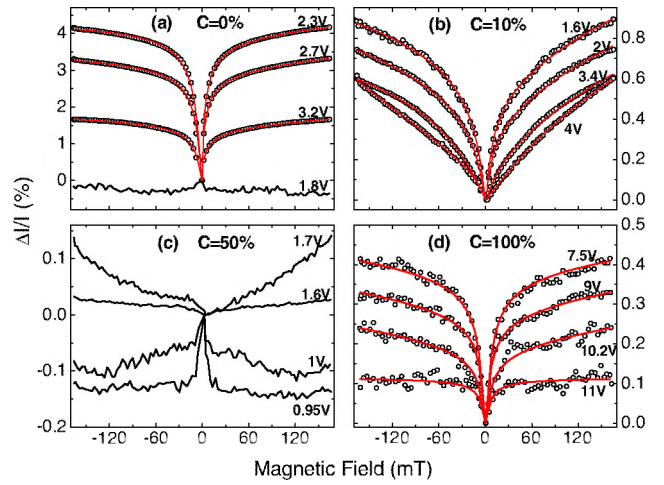

FIG. 1 (color online). Magnetoconductance (MC) response, $\Delta I/I$ vs field, B in unblended diodes $c = 0$ (a) and $c = 100\%$ (d), and OPV devices (b) and (c) based on blends of MEH-PPV/PCBM with various PCBM concentrations, c (in weight) and biasing voltage, V, at room temperature. The red lines through the data points are fits using a two-mechanism model for the spin-mixing process (see text).

the unblended devices (both $c = 0$ [panel (a)] and $c = 100\%$ [panel (d)] can be approximately fit by an empirical relation [1]: $f(B, B_0) \sim B^2/(|B| + B_0)^2$ at both positive and negative MC values. However, for $c = 10\%$ the MC response is less strongly field dependent at all V's; it is thus clear that the positive HF component dominates the MC response in the blends. We note that the HF component also exists in the unblended devices; however, it is difficult to observe due to the strong LF component. (iv) Finally the positive LF component completely disappears from the MC response in the $c = 50\%$ device [Fig. 1(c)]. We found instead, a very small negative MC at low V, followed by a small positive HF response at large V.

Figure 2(a) summarizes the MC value, defined as $\Delta I/I_{\max} = [I(160) - I(0)]/I(0)$ (see Fig. 1) vs V in four devices with various c [17]. For $c = 0, 1\%$, and 10% the MC first increases, saturates and then decreases with V. This response is in contradiction with the bipolaron model [6], since at large V we expect *larger* P^+ and P^- concentrations; and, consequently, an increase of bipolarons density is anticipated, but is not observed. Also as seen in Figs. 1 and 2 the MC is very small in the $c = 50\%$ device, where phase separation of the polymer and fullerene constituents is known to exist [16]. This shows that the positive MC is due to both P^+ and P^- together in the active layer, permitting PP formation [3]. We also note that the bias voltage onset, V_0 (= 1.7 volt) for the positive LF MC component in the $c = 0$ device coincides with the appearance of EL, showing exciton formation from PP's, and this also favors the exciton model [3]. Clear evidence in support of this interpretation is that in all devices the MEL response basically follows the LF MC component, rather than the negative, or the HF components. This is shown in
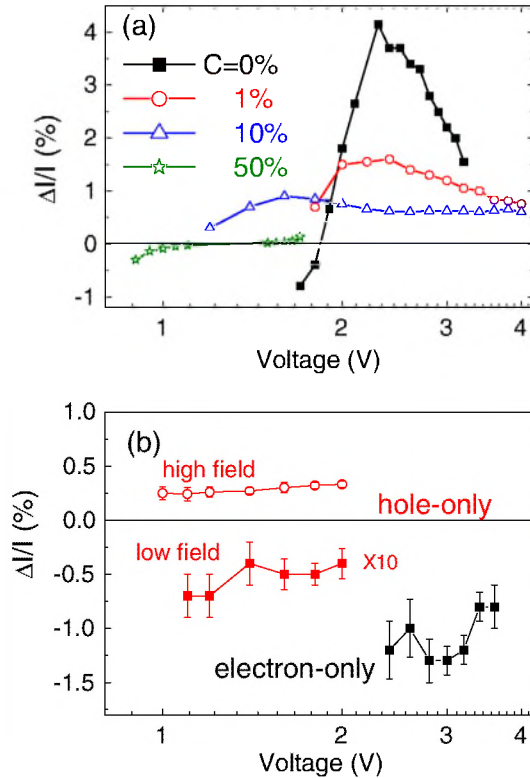
FIG. 2 (color online).   (a) The room temperature MC value at $B = 160$ mT, namely $[I(160 \text{ mT}) - I(0)]/I(0)$ as a function of the biasing voltage, V for MEH-PPV devices at four PCBM concentrations, c. (b) Same as in (a) but for unipolar MEH-PPV devices at 6 K; electron-only (black squares) and hole-only red circles for HF, and red squares for the LF components (multiplied by a factor of 10).
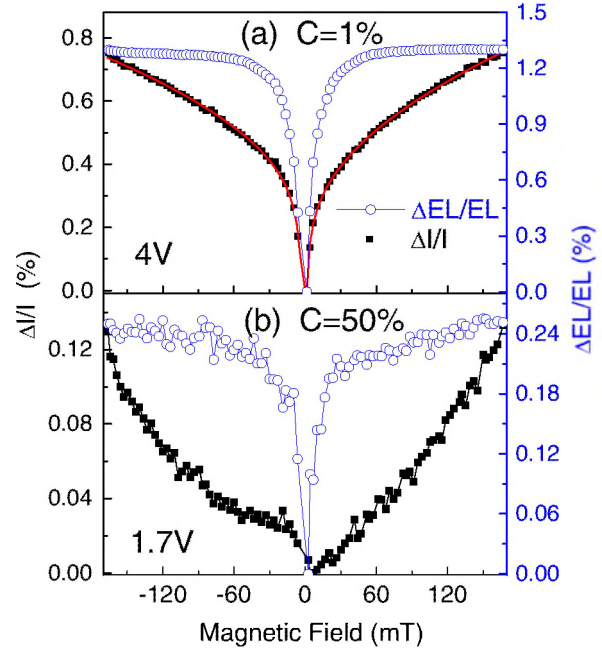

FIG. 3 (color online).   Comparison between MEL (blue circles; right axis) and MC (black squares; left axis) responses in MEH-PPV/PCBM OPV devices at two PCBM concentrations and biasing voltages; (a) $c = 1\%$, $V = 4$ volt; (b) $c = 50\%$ $V = 1.7$ volt. The red line through the data points are fits using the two-mechanism model as in Fig. 1 (see text).

Fig. 3, where we compare the MEL and MC responses in devices with $c = 1\%$ and 50%, respectively. It is seen that the MEL response is positive at all c, and is much narrower than the MC response; it follows the positive LF component even in the $c = 50\%$ device, where the EL is very small anyhow. This characteristic MEL behavior attests that the main MC response in the unblended devices is caused by spin-mixing of tightly bound PP's via the HFI [3,4].

For understanding the novel positive HF MC response that is revealed in the blends we note that this component also decreases with blending; therefore is also related to PP's in the active layer. However, it does not correlate well with the MEL response (Fig. 3), and therefore is due to a different PP type; most probably charge transfer (CT) pair across the polymer-fullerene interface, with P^+ in the polymer chain and P^- in the fullerene molecule [18]. Such CT pair does not luminesce in the visible spectral range, and hence cannot contribute to MEL. However since P^+ and P^- in the CT pair are each influenced by different environment, they possess different giromagnetic $(g-)$ factors, namely $g^+ \neq g^-$ (i.e. $\Delta g \neq 0$) [19]; and therefore a new mechanism for spin-mixing with B becomes avail-

able. This process was dubbed in the MFE literature as the Δg mechanism [12,20]; which shows a response given by $g(B) = [B/B^*]^{1/2}$ [21], where B^* is of order 5 T [20,21].

We therefore fitted the MC response in the blends with the two proposed spin-mixing mechanisms, namely, the HFI-mechanism for the LF component, and the Δg-mechanism for the HF component [21], respectively; using the relation: $\text{MC}(B) = a^* f(B, B_0) + b^* g(B)$, where a, b and B_0 are free parameters (see Figs. 1 and 3). In the unblended devices for $c = 0$ [Fig. 1(a)] we found that $B_0 = 3.5$ mT, whereas a/b ratio is about 3 at $V = 2.3$ volt, and continuously decreases with V in agreement with the decrease of the LF component with V seen in Figs. 1 and 2; whereas for $c = 100\%$ [Fig. 1(d)] we found $B_0 = 2.5$ mT [22], and a similar decrease in a/b ratio with V. For $c = 1\%$ (Fig. 3) and $c = 10\%$ [Fig. 1(b)]; however, the a/b ratio decreases by an order of magnitude, showing the dominance of the HF component due to the 'Δg-mechanism' in the MC response; whereas B_0 increases somewhat to ~ 5 mT. For the MEL fit (Fig. 3) a/b ratio remains large (~ 4) showing that this MFE still originates from PP's in the polymer phase of the blends.

For understanding the negative MC response seen in most devices at low V (Fig. 1), we study MFE in hole- and electron-unipolar $c = 0$ devices. In both devices we observed (Fig. 4) a *negative* LF MC that does not depend much with V [Fig. 2(b)]. Therefore, this response agrees with spin-mixing in hole- and electron-bipolaron species,
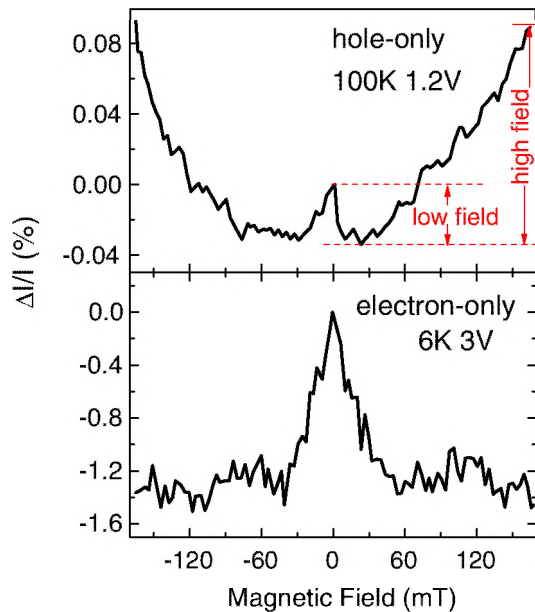
FIG. 4 (color online). MC response of unipolar MEH-PPV devices ($c = 0$) at 6 K. (a) hole-only diode at $V = 1.2$ volt, where the low-field and high-field components are defined; (b) electron-only diode at $V = 3$ volt.

rather than with neutral PP's. We also note that the MC response is much larger for the electron-unipolar device compared to that in the hole-unipolar device. This is in contrast with the MC response in Alq$_3$ unipolar devices [23], where the MC value was found to be much larger in hole-unipolar devices compared to electron-unipolar devices. In general bipolaron formation is not favorable in organic semiconductors and requires large relaxation energy to compensate the gain in energy due to the Coulomb repulsion. It may thus be that deep traps are involved in bipolaron formation, such as trions [24] for example. Deep traps are more abundant for *minority* carriers, which are therefore less mobile [10]. This explains the larger MC negative response in electron MEH-PPV-based unipolar devices, in which electrons are the minority carriers; as opposed to larger MC response in hole Alq$_3$-based unipolar devices, where holes are the minority carriers [23].

The bipolaron model also explains the MC response of OPV devices at optimum blending, namely $c = 50\%$. Since the donor and acceptor phases are separated in this blend, then MC is governed by P^-P^- and P^+P^+ pairs in each constituent. P^-P^- pairs occur in the fullerene phase, where MC is quite weak [Fig. 1(d)]; thus the MC response in this blend is dominated by the P^+P^+ response in the MEH-PPV phase. This MC response is negative and very weak in hole-unipolar devices [Fig. 4(a)], consistent with the weak negative MC response for OPV with $c = 50\%$ [Fig. 1(c)].

In conclusion we studied MC and MEL in organic diodes of MEH-PPV/PCBM blends with various concentrations, c. We provide strong evidence for the existence of several MC components in this system. In the unblended devices we found that a positive low-field component dominates the MC response; this component is due to magnetic field change of the spin sublevels mixing via the HFI in PP species. However, in the blended OPV devices the MC response is dominated by a broader positive component that is due to changes in spin sublevel mixing of CT states, caused by Δg mechanism. Finally the negative MC component in both unipolar devices at $c = 0$ and $c = 50\%$ is caused by change in spin mixing of electron and hole bipolarons.

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