Magnetoconductance Response in Unipolar and Bipolar Organic Diodes at Ultrasmall Fields

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We measured magnetoconductance (MC) response in a number of *unipolar* and *bipolar* organic diodes based on π-conjugated polymers and small molecules at fields $|B| < 100$ mT and various bias voltages and temperatures. Similar to magneto-electroluminescence, the MC(B) response in bipolar diodes shows a sign reversal at ultrasmall $|B| < 1$–2 mT due to interplay of hyperfine and Zeeman interactions in opposite-charge polaron pairs. Surprisingly, similar MC(B) response was also measured in unipolar devices, indicating the existence of like-charge polaron pairs, however, with a clear difference between the hyperfine interaction constants of electron polaron and hole polaron.

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Organic magnetoconductance (MC), namely, the change in the organic diode electrical conductance under the influence of an external magnetic field, **B** [1–12] is one aspect of the broader research area of "magnetic field effect" (MFE) in the organics [13], which also includes magneto-electroluminescence (MEL) in organic light emitting diodes (OLEDs). Typically, the organic MC response has been observed in relatively low fields ($|B| <$ 100 mT) at various temperatures, having maximum value of $\sim$20% [14]. It has been generally accepted that the organic MFE originates from the field-induced change in the dynamics of long-lived radical spin pairs in solutions [13], or polaron pairs in organic solids and devices [9,10]. However various models have been proposed for explaining the MFE response in OLEDs. Most of these models are based on the hyperfine interaction (HFI) between the injected spin-$\frac{1}{2}$ carriers and nuclear spins in the organic semiconductor layer [5–10]. The most common model considers the HFI mixing of spin sublevels of polaron pairs, where spin singlet and triplet level-mixing becomes less effective as B increases [9]. Recently [15], by replacing protons (H) with deuterons (D) in the π-conjugated polymer interlayer, where the D-polymer has a smaller HFI constant, a_{HFI}, it was demonstrated that the HFI indeed plays a crucial role in the MFE of polymer OLEDs.

In this Letter we include in our study also very small fields ($|B| < 1$ mT) and extend our MFE measurements to a variety of unipolar and bipolar organic devices. We show that the MC(B) response in fact contains a peculiar sign reversal at $B < 1$–2 mT, similar to that reported earlier in the MEL response of a polymer OLED [15]. This ultrasmall MFE (or USMFE) component manifests itself as a MC sign reversal from positive (negative) to negative (positive) in bipolar (unipolar) devices, forming a dip (peak) at B_m that scales with the half-width at half-maximum (HWHM), ΔB, of the normal MC(B) response. We found, however that the USMFE in polymers has different width in electron- and hole-unipolar polymer diodes, indicating different hyperfine interaction constant for the electron-polaron and hole-polaron in these materials. We explain the complete MC(B) response using a model Hamiltonian based on "spin pairs" of loosely bound spin-$\frac{1}{2}$ polarons with small exchange, having HFI with several strongly coupled nuclear spins, which are opposite-charge for bipolar devices and like-charge for unipolar devices. The intermixing between the hyperfine-split spin sublevels increases at very small **B** due to level crossing at $B = 0$, thereby causing a MC sign reversal.

We have studied MC in organic diodes based on a variety of π-conjugated polymers and small molecule spacers. The polymers include: two derivatives of poly (phenylene-vinylene) (PPV), namely, 2-methoxy-5-(2'-ethylhexyloxy) (MEH-PPV), and three isotope enriched 2-methoxy-5-(2'-dioctyloxy) (DOO-PPV). The latter include H-DOO-PPV, D-DOO-PPV, and C13-DOO-PPV (^{13}C-carbon rich). The three isotope rich DOO-PPV polymers have different a_{HFI} since skeletal protons (nuclear spin $I = 1/2$) are replaced by deuterium ($I = 1$) in D-DOO-PPV (causing smaller a_{HFI}); whereas some of the ^{12}C nuclei ($I = 0$, no HFI) are replaced by ^{13}C nuclei ($I = 1/2$ having substantial HFI), thus increasing the effect of the HFI. The small molecules that we studied include Alq_3, tetracene, pentacene, rubrene, and several fullerenes [only a subset is shown here in Fig. 1]. We fabricated organic diodes from all of these materials, and subsequently measured the MC response with high-field resolution at various bias voltages and temperatures. In bipolar devices we also measured MEL(B) with very similar response as MC(B). By shielding the measuring apparatus from the earth magnetic field ($B_E \approx 0.053$ mT in Utah) using mu-metal shield, we verified that the USMFE is not caused by B_E.

The devices used were 5 mm^2 area diodes, where the organic spacers were deposited onto a hole transport layer: poly(3,4-ethylenedioxythiophene) (PEDOT)-poly(styrene sulphonate) (PSS). For the bipolar devices we capped

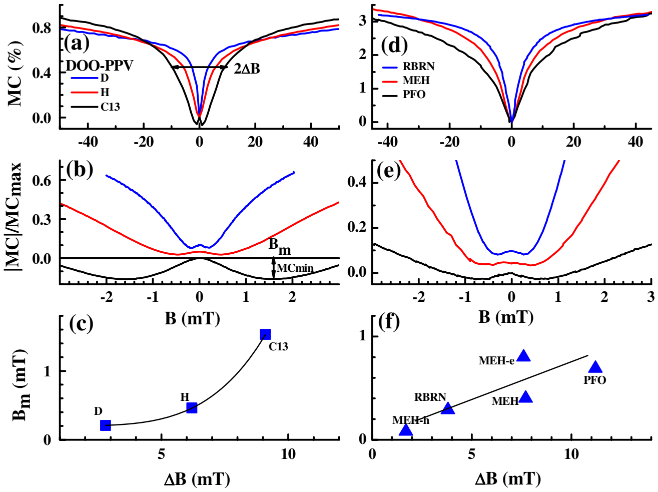

FIG. 1 (color online). MC response vs field, B in bipolar organic diodes based on: (a)–(c) three isotopes of DOO-PPV; (d)–(f) MEH-PPV, PFO (MC × 3), and rubrene RBRN; (MC × 8). Panels (a) and (d) show MC(B) for $|B| < 50$ mT; whereas panels (b) and (e) show the *normalized* MC(B) measured with high-field resolution, for $|B| < 3$ mT (some MC responses are shifted vertically for clarity); $\mathrm{MC}_{\max}$ is the saturation MC value at large B. ΔB is the HWHM for the normal MC(B) response, as defined in (a); whereas $\mathrm{MC}_{\min}$ and B_m are for the USMFE response, as defined in (b). Panels (c) and (f), respectively, summarize B_m vs ΔB for the MC(B) responses in (a) and (b), and (d) and (e); the straight lines are guides for the eye. Panel (f) also summarizes the USMFE response of electron-only MEH-*e* and hole-only MEH-*h* unipolar devices based on MEH-PPV [MC(B) shown in Fig. 2].

the bilayer structure with a transparent anode: indium tin oxide (ITO), and a cathode: calcium (protected by aluminum film). For MEH-PPV we also fabricated *unipolar* devices: the hole-unipolar device was in the form of ITO/PEDOT-PSS/MEH-PPV/Au; whereas the electron-unipolar device was Al/LiF(~2 nm)/MEH − PPV/Ca/Al. The organic diodes were transferred to a cryostat that was placed in between the two poles of an electromagnet producing fields up to ~300 mT. The devices were driven at constant bias, V, using a Keithley 236 apparatus; and the current, I, was measured while sweeping B. We define MC(B) by the relation, $\mathrm{MC} \equiv [I(B) - I(0)]/I(0)$, so that increasing current with B is interpreted as *positive* MC.

Figure 1(a) shows the MC(B) response of several bipolar diodes for $|B| < 50$ mT at room temperature and $V > V_{BI}$, where V_{BI} is the device built-in potential at which both positive and negative charges are injected into the active layer [7]. For $|B| > \sim 2$ mT, the MC(B) response is positive, reaching a saturation level, $\mathrm{MC}_{\max}$ at large B. This is the *normal* MC(B) response [1–10] that is characterized by HWHM, ΔB ranging from 2.8 mT for D-DOO-PPV, to 6.2 mT for H-DOO-PPV, to 9.1 mT for ^{13}C-rich DOO-PPV [Fig. 1(c)]. The isotope-dependent ΔB (where ΔB increases with a_{HFI}) for the three DOO-PPV polymers shows that the HFI indeed plays a crucial role in determining the MC response in polymeric organic diodes, as reported in [15] for the EL(B) response. The USMFE component observed earlier in MEL(B) [15], is also demonstrated here in the MC(B) response [Fig. 1(b)]. As clearly seen, upon decreasing B the MC reverses sign, reaching a minimum ($\mathrm{MC}_{\min}$) at $B = B_m$, before increasing again toward $B = 0$. The USMFE response component was obtained in most organic devices based on various polymers and small molecules; the MC(B) responses of three additional devices are shown in Fig. 1(d). When the USMFE response is summarized by plotting B_m vs ΔB [Figs. 1(c) and 1(f)], it is apparent that B_m increases with ΔB (i.e., with larger a_{HFI}).

The USMFE response is not limited to bipolar devices. In Fig. 2 we show MC(B) responses of hole-only and electron-only MEH-PPV diodes; similar responses were measured for DOO-PPV unipolar devices (not shown here). The high-field MC in unipolar devices is *negative* [Fig. 2(a)] [10], and thus the USMFE response appears here as negative-to-positive sign reversal with a *maximum* at $B_m \sim 0.8$ mT for the electron-only device, and $B_m \sim 0.1$ mT for the hole-only device [Fig. 2(b)]. Importantly, ΔB is smaller in the hole-only device compared to that in the electron-only device; this is consistent with *smaller* a_{HFI} for hole polaron than for electron polaron in MEH-PPV, in agreement with recent measurements using transient spin response [16]. We therefore conclude that B_m increases with ΔB in unipolar devices similar to bipolar devices, and thus also include the USMFE in unipolar devices in the summary shown in Fig. 1(f).

The USMFE response depends on both bias voltage and temperature; an example is shown in Fig. 3 for D-DOO-PPV. At 10 K we found that $|\mathrm{MC}_{\min}|$ decreases by a factor of 2 as the bias increases from 3.4 to 4.4 V, whereas B_m does not change much. At $V = 3.4$ V we found that $|\mathrm{MC}_{\min}|$ increases as the temperature increases from 10 to 300 K, whereas B_m is not affected by the temperature. Importantly, the dependence of $\mathrm{MC}_{\min}$ on V and T is found to follow the same dependencies as the saturation value, $\mathrm{MC}_{\max}$; therefore the ratio, $\mathrm{MC}_{\min}/\mathrm{MC}_{\max}$ is *independent* on V and T [Fig. 3 insets]. This indicates that the USMFE component is *correlated* with the normal MC response, and thus is also determined by the HFI. We thus conclude that any viable model describing the normal MC(B) response needs to also explain the USMFE response component.

In the traditional view of organic MC in OLED the injected spin-$\frac{1}{2}$ carriers form weakly bound polaron spin pairs (or SP), in either singlet $(\mathrm{SP})_S$ or triplet $(\mathrm{SP})_T$ spin configuration that precedes electroluminescence emission by intrachain singlet excitons. As B increases, the intermixing between the SP singlet and triplet spin configurations decreases due to the increased Zeeman contribution, thereby affecting their respective populations; this leads to a monotonous, $\mathrm{MC}_M(B)$ response [9,10]. However, if the exchange interaction constant J is finite, then a new $\mathrm{MC}_{\mathrm{LC}}(B)$ component emerges at $B \approx B_{\mathrm{LC}} = J$, where a

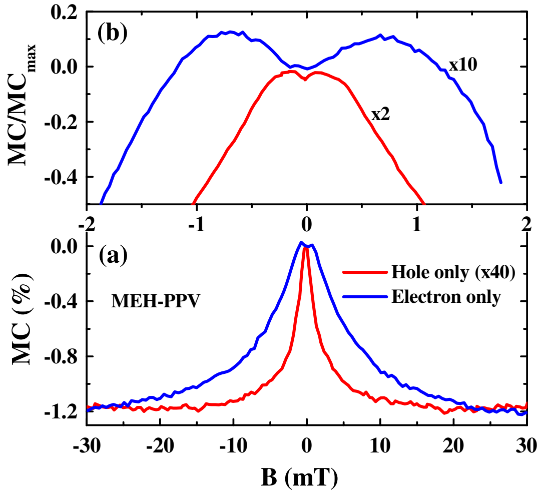

FIG. 2 (color online). Normalized MC(B) response for (a) $|B| < 30$ mT, and (b) $|B| < 2$ mT of hole- and electron-only *unipolar* diodes based on MEH-PPV, measured at room temperature and $V = 3$ and 20 V, respectively. The MC(B) responses are shifted in (b) for clarity.

singlet-triplet level-crossing (LC) occurs giving rise to *excess* spin intermixing between the singlet and triplet SP manifolds. The MC$_{\text{LC}}$(B) component has therefore an *opposite* sign with respect to the regular MC$_M$(B) response, which results in a strong MC(B) modulation response at $B = B_{\text{LC}}$ [13]. By explicitly taking into account the HFI between each of the SP constituents and N (≥ 1) strongly coupled neighboring nuclei, we can explain the USMFE component response as due to a LC response at $B = 0$.

Our model is based on the time evolution of the SP spin sublevels in a magnetic field [15]. For bipolar devices the SP species is the opposite-charge polaron pair, whereas for unipolar devices it is the like-charge π dimer (i.e., biradical, or bipolaron [6,10]). The SP spin Hamiltonian, $\mathcal{H}$, includes exchange interaction (EX), HFI, and Zeeman terms: $\mathcal{H} = H_{\text{Zeeman}} + H_{\text{HFI}} + H_{\text{ex}}$; where $H_{\text{HFI}} = \sum_{i=1}^{2}\sum_{j=1}^{Ni}[S_i \cdot \tilde{A}_{ij} \cdot I_j]$ is the HFI term, $\tilde{A}$ is the hyperfine tensor describing the HFI between polaron (i) with spin S_i ($= 1/2$), and N_i neighboring nuclei, each with spin I_j,; $H_{\text{Zeeman}} = g_1\mu_B BS_{1z} + g_2\mu_B BS_{2z}$ is the electronic Zeeman interaction component; g_i is the g factor of each of the polarons in the SP species (for simplicity $g_1 = g_2 = g$); μ_B is the Bohr magneton; $H_{\text{ex}} = J\mathbf{S}_1 \cdot \mathbf{S}_2$ is the isotropic exchange interaction; and the applied magnetic field $\mathbf{B}$ is along the $\mathbf{z}$ axis. An example of the spin energy sublevels dispersion with B using $\mathcal{H}$ for $N_1 = N_2 = 1$, and nuclear spin $I = 1/2$ (namely, overall 16 energy levels) is shown in Fig. 4(a). Note the multiple LCs that occur at $B = 0$; other LCs appear at larger B, but those are between mostly triplet sublevels, and thus hardly change the singlet-triplet (S-T) intermixing rate and consequent populations.

The steady state SP$_S$ and SP$_T$ populations are determined by the spin-dependent generation and decay rates. The effective decay rate constant, k is composed of dissociation rate (that contributes to the device current density [17]) and recombination rate (for bipolar diodes); these two processes eliminate the SP species. The SP spin sublevel populations are also determined by the S-T intermixing provided by the HFI. Any change of the S-T intermixing rate, such as produced by increasing $\mathbf{B}$ may perturb the overall relative steady state spin sublevel populations; and through the SP dissociation mechanism it may consequently contribute to MC(B). To obtain sizable MC value, $k < a_{\text{HFI}}$. The USMFE response in this model results from the strong coherent S-T interconversion of

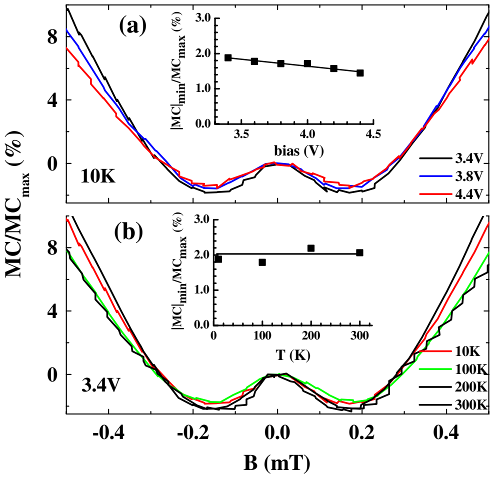

FIG. 3 (color online). Normalized MC(B) response of a bipolar diode based on D-DOO-PPV for $|B| < 0.5$ mT at (a) various bias voltages at $T = 10$ K, and (b) various temperatures at $V = 3.4$ V; MC$_{\text{max}}$ is defined in Fig. 1. The insets in (a) and (b), respectively, summarize MC$_{\text{min}}$/MC$_{\text{max}}$ at various voltages at 10 K, and various temperatures at 3.4 V.

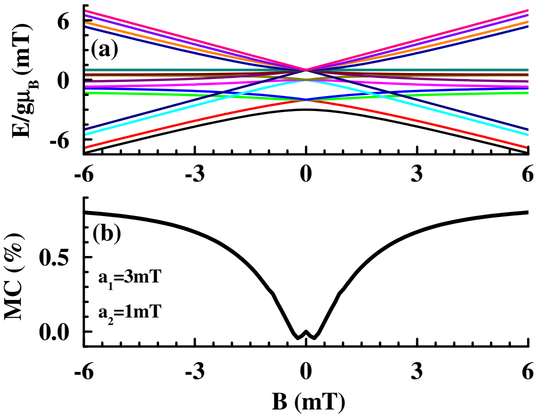

FIG. 4 (color online). (a) Example of calculated energy levels vs B for a spin pair with isotropic HFI; $a_1/g\mu_B = 3a_2/g\mu_B = 3$ mT, $J = 0$. Note the multiple level crossing at $B = 0$. (b) Calculated MC(B) response for a SP with axially symmetric HFI averaged over all magnetic field directions. The isotropic HFI is the same as in (a). The anisotropic HFI is $a_{zz} = 0.15a_i$ for the respective SP constituent.

nearly degenerate levels at $B \ll a_{\mathrm{HFI}}/g\mu_B$, where a_{HFI} is the isotropic HFI constant.

The relevant time evolution of the S-T intermixing that determines the steady state SP_S population is obtained in our model via the time-dependent density matrix $\rho(t)$. Solving $\mathcal{H}$ for the energies E_n and wave functions Ψ_n, and starting from a singlet state we express the time evolution of the singlet population $\rho_S(t)$ as [13,18]

$$\rho_S(t) = \mathrm{Tr}[\rho(t)P^S] = (4/M)\sum_{m,n=1}^{M} |P^S_{mn}|^2 \cos\omega_{mn} t, \quad (1)$$

where $P^S{}_{mn}$ are the matrix elements of the singlet projection operator, $\omega_{mn} = (E_n - E_m)/\hbar$, and M is the number of spin configurations included in the SP species (for $I = 1/2$, $M = 2^{N+2}$). In the absence of SP decay, Eq. (1) contains many rapidly oscillating terms that do not contribute to the singlet steady state population, and two important terms that do not oscillate in time. These are $\langle\rho_S(t=\infty)\rangle = 4\sum_m |P^S{}_{mm}|^2/M + 4\sum_{m\neq n}|P^S{}_{mn}|^2/M$, where the second summation is restricted to *accidental degenerate levels*, for which $\omega_{mn}(B) = 0$. The first (diagonal) term contributes to the "normal" monotonous $\mathrm{MC}_M(B)$ response, whereas the second ("level crossing") term contributes to $\mathrm{MC}_{\mathrm{LC}}(B)$ response that modulates $\langle\rho_S(t=\infty)\rangle$ primarily at $B = 0$, where the S-T degeneracy is relatively high [see Fig. 4(a)]. The combination of $\mathrm{MC}_M(B)$ and $\mathrm{MC}_{\mathrm{LC}}(B)$ components at $B \sim 0$, in principle, explains the USMFE response in organic devices.

When the SP species decays, $\rho_S(t)$ in Eq. (1) needs be multiplied by a decay function $f(t)$. Under these conditions the steady state singlet decay yield, $\Phi_S \equiv k\int_0^\infty \rho_S(t)f(t)dt$ is given by

$$\Phi_S(B) = (4/M)\sum_{n,m=1}^{M} |P^S_{mn}|^2 f(\omega_{mn}) \quad (2)$$

where$f(\omega) = k\int_0^\infty \cos\omega t f(t)dt$. When SP_S elimination is controlled by an exponentially decaying function $f(t) \propto \exp(-kt)$, we have $f(\omega) = k^2/(k^2 + \omega^2)$.

The triplet yield in this model is given by, $\Phi_T(B)$ $[= 1 - \Phi_S(B)]$ [15]. If the SP singlet and triplet dissociation rates into free polarons are equal to each other, then their relative contribution to the device conductivity would not change with B in spite of their field-induced population change, resulting in null MC(B) response. We account for the dissociation rate difference by expressing MC(B) as the weighted average [15]:

$$\mathrm{MC}(B) = \frac{\Phi_S(B) + \delta_{TS}\Phi_T(B)}{\Phi_S(0) + \delta_{TS}\Phi_T(0)} - 1, \quad (3)$$

where $\Phi_S(B)$ is given by Eq. (2) and δ_{TS} is the triplet-singlet "symmetry breaking" parameter that describes the relative S-T contributions to the device conductance via dissociation into free polarons.

Figure 4(b) shows the calculated MC(B) response using Eqs. (1)–(3) for an axially symmetric anisotropic HFI with $N_1 = N_2 = 1$ ($I = 1/2$; $M = 16$), where $a_{\mathrm{HFI}}(\mathrm{electron}) = 3a_{\mathrm{HFI}}(\mathrm{hole}) = 3$ mT (in units of $g\mu_B$), $J = 0$, $\delta_{TS} = 0.96$, and an exponential SP decay $\hbar k/a_{\mathrm{HFI}}(e) = 0.001$. The calculated MC($B$) response captures both the obtained USMFE response at small B, as well as the approximate $B^2/({B_0}^2 + B^2)$ shape at larger B, where $B_0 \approx 1.5a_{\mathrm{HFI}}(e) \approx 4.5$ mT. The excellent agreement between theory and experiment, including both B_m and USMFE shape and relative amplitude, validates the model used.

In summary, we demonstrate that the peculiar USMFE component at $B \ll a_{\mathrm{HFI}}/g\mu_B$ that was reported before for MEL in bipolar polymer OLED [15], is in fact generic for many MFE responses including MC(B) of bipolar and unipolar diodes. Our model explicitly includes in the SP spin Hamiltonian the HFI with the most strongly coupled nuclear spins, and is capable of reproducing the entire MC(B) response, including the USMFE component.

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