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Large magnetic field effects in electrochemically doped organic light-emitting diodes

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Large negative magnetoconductance (MC) of ~12% is observed in electrochemically doped polymer light-emitting diodes at sub-band-gap bias voltages ($V_{bias}$). Simultaneously, a positive magnetoefficiency ($\eta$) of 9% is observed at $V_{bias} = 2$ V. At higher bias voltages, both the MC and $\eta$ diminish while a negative magnetoelectroluminescence (MEL) appears. The negative MEL effect is rationalized by triplet-triplet annihilation that leads to delayed fluorescence, whereas the positive $\eta$ effect is related to competition between spin mixing and exciton formation leading to an enhanced singlet:triplet ratio at nonzero magnetic field. The resultant reduction in triplet exciton density is argued to reduce detrapping of polarons in the recombination zone at low-bias voltages, explaining the observed negative MC. Regarding organic magnetoresistance, this study provides experimental data to verify existing models describing magnetic field effects in organic semiconductors, which contribute to better understanding hereof. Furthermore, we present indications of strong magnetic field effects related to interactions between trapped carriers and excitons, which specifically can be studied in electrochemically doped organic light-emitting diodes (OLEDs). Regarding light-emitting electrochemical cells (LECs), this work shows that delayed fluorescence from triplet-triplet annihilation substantially contributes to the electroluminescence and the device efficiency.

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I. INTRODUCTION

Light-emitting electrochemical cells (LECs) are subspecies of organic light-emitting diodes (OLEDs) that consist of a single active layer in which mobile ions are admixed to an organic semiconductor.1–5 The addition of these ions results in a rather complicated device operation. In the presence of an electric field, these ions redistribute and pile up at the contacts. The resultant space charge of these so-called electric double layers (EDLs) leads to relatively large interfacial electric fields that can improve injection from contacts with large injection barriers. The electronic charge carriers that are injected from the contacts lead to a further redistribution of ions to compensate for the introduced electronic space charge. This process is called electrochemical doping and allows for relatively large carrier densities in LEC as opposed to OLEDs.6–13

In the field of organic magneto resistance (OMAR), LECs have only scarcely been studied as opposed to OLEDs. In OLEDs, transport typically takes place by hops through a percolating pathway. Typically, this pathway is the optimal transport channel, which is in actuality influenced by charge traps. In LECs, on the other hand, charge trapping is dominant in the form of electrochemical doping. Ions electrostatically compensate electrons or holes, resulting in effective Coulomb traps. In this paper, we show that this charge trapping is especially dominant at low bias voltages equal to or smaller than the band gap of the semiconductor. Therefore LECs can be regarded as an ideal test bed to study OMAR effects on trapped charges.

OMAR in LECs biased above the semiconductor band gap has been reported by Vardeny et al.14 They observed a positive magnetoconductance (MC) of ~0.4% and magnetoelectroluminescence (MEL) of ~5%. The results were explained by the polaron pair model.15 The difference in MC and MEL was attributed to imbalanced device characteristics regarding carrier injection and/or transport. As a result, a relatively large part of the current does not contribute to electroluminescence, leading to MC being smaller than MEL.

Here, we report on OMAR in Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) LECs. Large negative MC effects (~12%) are observed at $V_{bias} < E_{gap}$ after prolonged biasing at $V_{bias} = 4.0$ V. Simultaneously, a positive effect in the magnetoefficiency ($\eta$), determined by MEL–MC, is observed when electroluminescence (EL) is detectable. Both effects are low magnetic field effects (LFE) that are best described by a “non-Lorentzian”16 lineshape with a width of $B_0 = 2.2$ mT. The magnetic field effect (MFE) in efficiency is described by the two-site model previously reported by Kersten et al.,17 which models the competition between hyperfine field induced spin mixing and exciton formation. The MFE in current is rationalized as an indirect effect of the enhanced singlet:triplet ratio: long-living triplet excitons can detrack carriers from doping sites and hence indirectly enhance the current. Especially after conditioning and in the low-voltage regime, the number of trapped polarons is expected to be large. Next to both low-field effects, also a negative high-field effect (HFE) in the EL was observed at relatively large bias voltages. This effect is attributed to field dependent triplet-triplet annihilation that is found to have a significant contribution to the electroluminescence in LECs.

II. EXPERIMENT

The LECs in this study consist of an active layer of ~200 nm sandwiched between an indium tin oxide (ITO) and an aluminum electrode. The active layer is a blend of materials spin-coated from solution. This blend was prepared by mixing of the following 10 mg ml$^{-1}$ stock solutions in a mass ratio of 1:1.35:0.25: Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) in chloroform, poly(ethylene oxide) (PEO) in cyclohexanone and potassium triflate (KCF$_3$SO$_3$) in cyclohexanone. The aluminum electrodes were thermally deposited in a deposition chamber.
in a glovebox under a vacuum of $\sim 10^{-6}$ mbar. All device manufacturing and characterization was done under nitrogen atmosphere. The active area of the device, defined by a shadow mask, was 0.091 cm$^2$. The current-voltage characteristics were measured by a Keithley 2400 sourcemeter.

For MC and MEL measurements, a magnetic field perpendicular to the device was used. Current and electroluminescence (EL) were simultaneously measured at a constant bias voltage ranging between 0 and 4 V while the magnetic field was swept from 0 to 500 mT. The MC and MEL were determined by the relative change in current and EL: $MC = (I_B - I_{B=0})/I_{B=0}$ and $MEL = (EL_B - EL_{B=0})/EL_{B=0}$. $\eta_B$ was determined by the difference between MEL and MC: $\eta_B = (\eta_E - \eta_{B=0})/\eta_{B=0} \equiv MEL - MC$. Three magnetic field sweeps were performed at each bias voltage to account for temporal drift in the current and electroluminescence. Electroluminescence was measured by a Hamamatsu Si photodiode S1337-33BQ connected to a Keithley 6430 sub-Femtoamp remote source meter.

### III. EXPERIMENTAL RESULTS

Initially, the pristine LECs were studied by measurement of current-voltage and luminance-voltage characteristics (IVLs) in combination with MC-voltage measurements at magnetic field strengths $B \approx 0$ and 83 mT. The results are displayed in Figs. 1(a) and 1(b) (open symbols) and show typical LEC behavior: turn-on of electroluminescence for $V_{bias} \approx 4$ V. After this so-called conditioning, the device was set back to $V_{bias} = 0$ V followed by another measurement of an IVL characteristic shown in Fig. 1(a) (closed symbols). An enhancement of the current is mainly observed at bias voltages at and below $E_g$. Furthermore, electroluminescence was observed already at voltages lower than 2.4 V: for $2.1 \text{ V} < V_{bias} < 2.4 \text{ V}$. The current is also observed to change sign at $V_{bias} \approx 0.3 \text{ V}$ instead of 0.0 V. This can be related to slow discharging of the LEC after conditioning.

An MC measurement on the conditioned device is shown in Fig. 1(b) (closed symbols). A negative MC has appeared for bias voltages below the semiconductor band gap with a minimum value of roughly $-10\%$. The strongest effect observed was $-12\%$ when replicating the measurements on similar devices. This large effect is by itself quite a spectacular observation. First of all, in ordinary OLEDs, OMAR is typically relatively small when biased below the bandgap. Furthermore the LEC is not optimized with respect to OMAR. In addition, the here reported value is among the largest MC reported in OLEDs.

The appearance of negative MC after conditioning is a temporal effect that persists for at least 1 hour after conditioning. After leaving the device unbiased for 12 hours, the effect has vanished. Conditioning again at 4.0 V for 30 minutes makes it reappear. The effect of conditioning can therefore be considered reversible (see Fig. S1 in Ref. 20).

MC and MEL measurements as a function of magnetic field strength are shown in Figs. 2(a) and 2(b), respectively. The MC curves were fitted using the modified Lorentzian expression $f(B, B_0) \sim B^2/(|B| + B_0)^2$ with a linewidth $B_0 = 2.2$ mT. The MEL curves were fitted with two modified Lorentzians with linewidths of $B_0 = 2.3$ and 220 mT, accounting for a low- and high-field effect, respectively. By subtracting the MC from the MEL, $\eta_B$ was determined and plotted in Fig. 2(c). In Fig. 2(d), values of MC, MEL, and $\eta_B$ in the limit of $B \rightarrow \infty$ are plotted together as a function of voltage. Additional experiments on LECs based on another type of PPV (superyellow) gave similar results, see Fig. S3 in Ref. 20.

### IV. DISCUSSION

#### A. Device physics

To facilitate discussion of the observed magnetic field effects, we will first briefly review the device operation of an LEC. In Fig. 3, schematics are shown of the carrier distributions and potential profiles in the LEC before, during, and after conditioning at $V_{bias} = 4$ V. In a pristine device, only ionic charges related to the salt are present as shown in Fig. 3(a). The binding energy of this salt is a few tenths of an eV, resulting in a fraction of the salt that is thermally dissociated and thus susceptible to external fields. At the contacts, the ions form thin electric double layers (EDLs) to compensate for the built-in voltage induced by the difference in electrode work functions.

If now a bias voltage is applied that exceeds the polymer band gap, larger EDLs are formed resulting in the formation of Ohmic contacts. Consequently, carriers are injected and form space charge in the bulk. This space charge attracts mobile ions of opposite charge, leading to the formation of doped regions as is shown in Fig. 3(b). In between the doped regions, the electrons and holes recombine forming an intrinsic region. In the intrinsic region, the carrier density and mobility are low compared to the doped regions. Therefore a relatively large fraction of the applied potential drops over the intrinsic region to maintain current conservation as is shown in Fig. 3(b). The corresponding relatively large field results in dephosphination of mobile ions from this junction region. This initial doping due to carrier injection is a fast process that occurs within a second.
FIG. 2. (Color online) (a) MC(B) and (b) MEL(B) measurements on a conditioned PPV-based LEC at different bias voltages (dots). (a) The MC(B) was fitted (lines) with one non-Lorentzian ($B_0 = 2.2$ mT). (b) The MEL(B) was fitted (lines) with two non-Lorentzians accounting for a low-field effect ($B_0 = 2.3$ mT) and a high-field effect ($B_0 = 220$ mT). (c) $\eta(B)$ as derived from the ratio of the fits shown in (b) and (a). (d) Values of the fitted MC(B), MEL(B), and $\eta(B)$ curves in the limit of $B \to \infty$ vs applied bias voltage. The amplitudes of the low- (LFE) and high- (HFE) field effects in the MEL are split up in two graphs.

and is determined by the mobility and density of mobile ions.\(^{21}\) Part of the salt, however, remains undissociated. If the bias voltage is switched off at this point, the device returns to more or less the pristine state: the injected charges

FIG. 3. Schematic of carrier distribution and potential profile in an LEC (a) before, (b) and (c) during and (d) after operation. The carrier distributions for relatively short and long times of operation are shown in (b) and (c), respectively. The different types of carriers are indicated with their initials: a (anion), c (cation), e (electron), and h (hole).
either recombine or move back towards the electrodes whereas the ions redistribute to compensate each other electrostatically. If, alternatively, the bias is maintained, the remaining salt complexes have time to dissociate into mobile anions and cations. These are then as well separated from each other by moving into the $p$- and $n$-doped regions, respectively, as shown in Fig. 3(c). This slow doping process is dominated by the dissociation of salt complexes into ions rather than by the ion mobility. As a result, the doping process saturates in the order of minutes instead of within a second.\(^{21}\) Experimentally, this slow saturation is demonstrated by a continuous increase of current while the efficiency decreases. The efficiency decrease is related to exciton quenching at doping sites.\(^{22}\)

This quenching is an interaction between singlet excitons and trapped charges. It is typically a strong effect in LECs, as $p$-$i$-$n$ junction formation allows for relatively large numbers of carriers close to a narrow recombination zone. As triplet excitons typically live longer than singlet excitons, interactions between triplet excitons and trapped charges are likely present as well, although they cannot be directly observed in the efficiency. Such interactions will, however, prove to be important for the OMAR effects described later in this paper.

When removing the bias voltage after such a long transient, again the excess electronic carriers will recombine or be collected by the electrodes. However, as the doping density is maximized in this case, a larger amount of doping is expected to remain trapped inside the device as illustrated in Fig. 3(d). The difference in quasi-Fermi levels of the $p$- and $n$-doped regions then leads to a compensating electric field in the junction region. In planar cells, it has been observed that the sign of the electric field in the junction region changes after removal of the bias voltage.\(^{9}\) This is drawn in Fig. 3(d). During operation, the electrons and holes cause uncompensated space charge in the junction region. After switch-off, the electrons and holes recombine, leaving anions and cations to form space charge in this region. The anions and cations in the junction region either originate from ions that were already trapped in this region or ions that entered the junction region by drift and/or diffusion. In either case, the removal of the bias voltage leads to a switch in sign of the polarity of the electric field in the $p$-$i$-$n$ junction. In this state, the electronic transport is strongly influenced by the Coulomb traps formed by the ions in the $p$-$i$-$n$ junction. This is an interesting case for studying OMAR as charge traps are known to enhance the magnitude of OMAR in general.\(^{23}\)

The magnetic field effects reported in this paper are rationalized in the next sections in the light of the device physics explained above. In short, conditioning changes the device operation in the voltage regime at and below the semiconductor band gap. In a conditioned device, the active layer contains ions that trap electronic charges as well as uncompensated ions acting as Coulomb traps.

**B. Magnetic field effects**

The magnetic field effects observed in Figs. 1(b) and 2 can be separated by their respective linewidths: an MC and MEL effect with $B_0 \approx 2.2$ mT and an MEL effect with $B_0 \approx 220$ mT. The low-field effects arise at magnetic fields that are similar in size as that of the hyperfine fields, which are mainly caused by the surrounding hydrogen nuclei. In the absence of an external magnetic field, these hyperfine fields are randomly oriented, enabling spin mixing of nearby carriers. Sufficiently large external fields on the other hand reduce spin mixing. In literature, several models have been proposed in which hyperfine interactions are relevant for electron-hole interactions\(^{17,24,25}\) or electron-electron and hole-hole interactions.\(^{26,27}\)

To first give an overview of all, for this case, relevant processes regarding electronic charge transport and recombination, a schematic was drawn in Fig. 4. The schematic starts from free electrons and holes. When a free charge comes in the vicinity of another charge of equal polarity, a polaron pair is formed with either singlet or triplet character. As both carriers are on different sites, hopping through the semiconductor can lead to spin mixing, which is induced by the presence of random hyperfine fields. Both charges can, however, only arrive at the same site if the polaron pair has a singlet spin-state. In that case, a bipolaron is formed. Polaron pairs and bipolarons also dissociate, leading again to free electrons or holes.

Free electrons and holes can also meet each other and form electron-hole pairs with either singlet or triplet character. This process is favored by Coulomb attraction, which is rather strong in organic semiconductors due to the relatively low dielectric constant. The spin state of the electron-hole pairs can again be mixed by hopping through the semiconductor having random hyperfine fields. In case when the electron and hole arrive on the same site, an exciton is formed with a fixed spin state. In case when the exciton does not interact with any surrounding particles, the exciton will ultimately decay to the ground state.

In this paper, only the following interactions involving excitons are considered: triplet-triplet annihilation, which is
not shown in Fig. 4, and triplet-polaron interaction. In the latter case, the triplet exciton and polaron form a doublet or a quartet spin state. The doublet and quartet manifold show a zero-field splitting and these spin states can be mixed. Ultimately, either the exciton-polaron complex dissociates in a triplet exciton and a polaron, or the complex decays by energy or charge transfer resulting in the loss of the exciton, whereas the polaron remains. Singlet exciton quenching on polarons is not considered in this work because of the orders of magnitude shorter singlet lifetime in PPV.

In Fig. 4, green arrows are drawn to indicate the magnetic field dependent transitions between polaron pairs of equal and opposite charges and between a combination of a triplet exciton and a trapped charge. In the next sections, these interactions are discussed in relation to the experimentally obtained magnetic field effects in conditioned LECs.

C. Low-field effects in efficiency

The nonzero $M_{\xi}$ shown in Figs. 2(c) and 2(d) indicates that by application of a magnetic field, a change in singlet:triplet ratio has been established. Such a magnetic field effect originates from magnetic-field dependent singlet-triplet interconversion within the electron-hole pair prior to exciton formation. To describe this effect, we used the two-site model that was recently introduced by Kersten et al.\textsuperscript{17} This model describes the exciton formation process by considering the final hop of an electron from the site where it resides to a site where a hole is residing, or vice versa. As electron and hole are on different sites, the spins of both carriers can change due to hyperfine mixing because the exchange coupling is relatively small. The rate of spin mixing is proportional to the hyperfine precession frequency: $\omega_{hf} = g \mu_B B_{hf} h$, where $g$ is the $g$ factor; $g \approx 2$ is taken in this case for both electrons and holes, $\mu_B$ is the Bohr magneton, and $B_{hf}$ is the strength of the hyperfine field. The exciton formation itself can be described by the hopping rates $k_T$ and $k_S$ that are slightly different for triplet (T) and singlet (S) exciton formation due to a difference in energy and wave function. Further details on this model can be found in Ref. 17.

The model is used to determine the parameters needed to obtain similar values of MC and $M_{\xi}$ as in the experiment. The maximal experimental value of MC, $-0.09$, was taken from Fig. 2(d) at $V_{bias} = 1.25$ V. The corresponding value for $M_{\xi}$ at the same bias voltage could not be determined, as the electroluminescence was below the detection limit in the experiment. Therefore a value of $M_{\xi} = 0.15$ is assumed, which can be deduced by extrapolation to $V_{bias} = 1.25$ V.\textsuperscript{28} The model was used to calculate the $M_{\xi}$ for different ratios (i) of the singlet and triplet exciton formation rates, $k_S/k_T$, and (ii) of the triplet exciton formation rate and spin mixing rate, $k_T/\omega_{hf}$. $M_{\xi}$ is plotted in a contour plot in Fig. 5(a) [3D representations are shown in Fig. S5(c) in Ref. 20]. From the contour plot, a set of parameters can be deduced for which $M_{\xi} \approx 0.15$. This set is indicated by the white dashed line in Fig. 5(a). As a check whether this set comprises realistic values of these parameters, we compared the obtained results with parameters reported earlier in pure MDMO-PPV: $k_S/k_T = 0.7$ and $k_T/\omega_{hf} = 1.1$.\textsuperscript{17} These parameters are close to the parameters obtained in the modeling here [see white arrow in Fig. 5(a)], proving that the model description for the $M_{\xi}$ effect is possible.

What is left to explain is the diminishing of the low-field effect in the efficiency at higher bias voltages as observed in Fig. 2(d): both the negative low-field MFE in current and the positive low-field MFE in electroluminescence decrease, resulting in a lowering of the low-field MFE in efficiency. This can be explained by a shift in the contour plot towards larger values of $k_T/\omega_{hf}$ starting at log $k_T/\omega_{hf} = 0$.\textsuperscript{10} In that case, $M_{\xi}$ is observed to be reduced. An increase of the parameter $k_T/\omega_{hf}$ is likely, as at low-bias voltages, the carrier density is low in the LEC, favoring localization of polarons and increasing the contribution of traps to transport. Especially at sub-band-gap voltages, ions in the junction region are expected to act as traps [see Fig. 3(d)] as their space charge is dominant in the junction region. This means that the mobility, which is related...
to the hopping rate $k_T$, is relatively low at sub-band-gap bias voltages. When increasing the bias voltage, the trap states fill up so that free polarons cannot relax into these states. This as well as the larger carrier densities lead to an enhanced carrier mobility, hence a larger hopping rate. As the hopping rate of polarons is related to the exciton formation rate, also the latter is enhanced by the larger bias voltage. Such an enhancement means a shift towards the right-hand side in the contour plot shown in Fig. 5(a), which implies a reduction in $\Delta \eta$ as well.

In summary, the two-site model shows that the observed low-field effect in $\Delta \eta$ at bias voltages around the band gap originates from an interplay between (i) a magnetic field dependent spin mixing rate, (ii) a singlet exciton formation rate, and (iii) a triplet exciton formation rate of an electron-hole pair. Suppression of spin mixing effectively favors exciton formation with the lowest rate, i.e., the singlet exciton formation, leading to an enhanced efficiency. The roll-off of $\Delta \eta$ at higher voltages is arguably due to an enhanced hopping rate, leading to an enhancement of both the singlet and triplet exciton formation rate whereas the spin mixing rate remains the same. As a consequence, the effects of spin mixing and the external magnetic field are reduced, leading to smaller values of $\Delta \eta$.

### D. Low-field effects in current

For the rationalization of the negative MC in conditioned LECs biased below the band gap, the following magnetic field dependent interactions were considered (see also Fig. 4): polaron pair interactions between equal carrier types, polaron pair interactions between unequal carrier types, the interaction between excitons and trapped charges, and the influence of the triplet exciton density on the dielectric constant.

1. Polaron pair with equal carriers

To determine whether magnetic field dependent polaron pair interactions between equal carrier types in the doped regions play a role in the observed MC, an electrochemical transistor similar to Ref. 31 was fabricated. In this transistor, either $n$- or $p$-type doping is established, excluding any excitonic or recombination effects. No MC effects were observed at any doping level (see Sec. 3 in Ref. 20). Also during and after dedoping no MC was observed. This strongly suggests that spin-related interactions between electrons and electrons or holes and holes in electrochemically doped and partially dedoped MDMO-PPV do not play a significant role in transport. Moreover, it excludes magnetic field dependent interactions between electronic and ionic species.

2. Polaron pair with unequal carriers

Another option to explain the MC is polaron pair interaction between unequal carrier types during exciton formation. This interaction can only occur if both electrons and holes are injected. Despite biasing the LEC with a bias voltage below the band gap, both types of carriers can still be injected. A sign that this is indeed the case is the $L$-$V$ characteristic of the conditioned device as opposed to the unconditioned device in Fig. 1(a). For $2.1 \text{ V} < V_{\text{bias}} < 2.4 \text{ V}$, the appearance of electroluminescence is observed in the conditioned device. For lower bias voltages, electroluminescence may still be present but lies below the detection limit of the diode. To further substantiate this statement, a 1D numerical drift-diffusion model was used to calculate carrier density, recombination and potential profiles in an LEC before ($V_{\text{bias}} = 1 \text{ V}$), during ($V_{\text{bias}} = 4 \text{ V}$), and after ($V_{\text{bias}} = 1 \text{ V}$) conditioning. These profiles are plotted in Figs. 6(a)–6(c). The trapping by dopants was simulated by first biasing the device at $4 \text{ V}$, followed by a short relaxation at $V_{\text{bias}} = 0 \text{ V}$ after which the ions were artificially immobilized in the model. The short time span at which the device has been biased at $0 \text{ V}$ determines the trapped doping density. Details regarding the numerical model can be found in Refs. 8 and 22 and is part of Supplemental Material. The profiles in Figs. 6(a)–6(c) show that due to the fixed doping [see Fig. 6(a)] and the formation of Ohmic contacts by $p$- or $n$-type doping [see Fig. 6(c)], recombination still takes place even though the device is biased ($V_{\text{bias}} = 1 \text{ V}$) below the band gap ($E_{\text{gap}} = 2.2 \text{ eV}$). In the case shown here, the recombination has been lowered by a factor $\sim 10^6$ compared to the case of $V_{\text{bias}} = 4 \text{ V}$. This is in line with the luminance being below the detection limit of the experimental setup.

The profiles in Figs. 6(a)–6(c) furthermore show that the vast majority of the injected carriers form excitons instead of being extracted by the contacts: electron and hole densities only overlap in the central region of the device. This means that exciton formation limits the current passing through the cell. This knowledge can be used to determine the magnetic field dependent interactions related to spin mixing and singlet/triplet exciton formation. Therefore it is possible to determine the magnetoconductance related to spin mixing and singlet/triplet exciton formation by using the two-site model presented in the previous section. As shown in Fig. 5(a), the absence of spin mixing induced by a magnetic field enhances the singlet:triplet ratio, as evidenced by a positive $\Delta \eta$. Reasonable values of $\Delta \eta$ were found for $k_S/k_T < 1$, see Fig. 5(a). Hence the total exciton formation rate decreases with magnetic field. This decrease leads to a reduced current, as the current is proportional to the exciton formation rate. In Fig. 5(b), a contour plot of the MC is shown. Here, the MC is calculated from the sum of the exciton formation rates weighted by the calculated singlet:triplet ratio. The black, dashed lines indicate the parameters at which $\Delta \eta = 0.09$ is obtained. The gray dashed line is copied from Fig. 5(a) to indicate the parameters at which $\Delta \eta = 0.15$. The corresponding values of the MC on the gray dashed line lie between $0.00$ and $-0.03$, i.e., $0\%$ to $-3\%$. This is not in line with the experimentally determined $-10\%$ [see Fig. 1(b)]. Therefore this mechanism cannot be the main cause of the observed MC effects.

3. Magnetic field dependent triplet density: Effect on triplet exciton-polarons interactions

So far, polaron pair interactions were studied by means of an electrochemical transistor and the two-site model. The results of these studies prove that the negative MC in LECs is not related to polaron pair interactions in the doped regions (electron-electron, hole-hole) or in the junction region (electron-hole). Therefore excitonic interactions may need to
be included. To obtain an effect on the current density, the excitons need to interact with polarons either in the doped regions or in the recombination zone. As excitons are only formed in the recombination zone, the interaction is most likely to take place in or just next to this region. Due to the relatively large lifetime of triplet excitons, most likely their interaction with polarons is dominant.\cite{Leclerc2013,Leclerc2014,Leclerc2015} The triplet exciton density itself is magnetic field dependent, which is followed from the change in singlet:triplet ratio as calculated in Fig. 5(a). Polaron in the intrinsic region are expectedly trapped in deep states because of their relatively low density for $V_{\text{bias}} < E_{\text{gap}}$ [see Fig. 6(a)] and due to uncompensated immobile ions that lead to the space charge in the junction region [see Fig. 6(c)].

The interaction relevant here is then recombination of a trapped polaron and a triplet exciton producing a molecule in the ground state and a polaron, as shown in the bottom right in Fig. 4. The recombination process can then lead to detrapping of the polaron either due to energy or charge transfer from the triplet exciton. Hence the triplet exciton density, which itself is magnetic field dependent, can effectively change the mobility of polarons and concurrently the current passing through the cell. Note that this effect would be absent in a nonconditioned device, as then no excitons are formed for $V_{\text{bias}} < E_{\text{gap}}$, and because of the lesser importance of trapping, see Sec. IV A. For $V_{\text{bias}} > E_{\text{gap}}$, the trap states will be filled, resulting in trap-free carrier transport. This reduces the effect of detrapping on the total current density. Hence the MC rolls off at higher bias voltages, which is indeed observed in Fig. 1(b). Note that OMAR experiments on LECs by Vardeny et al.\cite{Vardeny2010} did not show the negative MC as observed here. They found that during operation, electron and hole transport was asymmetric, leading to pinning of the recombination zone to one of the electrodes. Therefore bipolar injection can in that work argued to be absent for $V_{\text{bias}} < E_{\text{gap}}$, as either one of the doped regions has not developed properly during operation.

A remark is in place regarding a possible magnetic field dependence of triplet-polaron (T-P) interactions (see Fig. 4). If interactions between triplet excitons and trapped polarons indeed play a role, a high-field MFE is expected related to the zero-field splitting of the resultant doublet and quartet manifold.\cite{Leclerc2013} In anthracene, for example, the rate of triplet quenching by polarons was found to be magnetic field dependent.\cite{Leclerc2014,Leclerc2015} As MDMO-PPV is a singlet emitter, this effect cannot be observed in the electroluminescence. The reason why no high-field MFE in the current is observed is unknown to us.

To attempt to explain the absence of a high-field MFE, the following processes need to be considered: a triplet exciton can either decay to the ground state or form a triplet polaron pair if a (trapped) polaron is near. The triplet-polaron pair either dissociates again in a triplet exciton and a polaron or the triplet exciton is quenched, leading to a molecule in the ground state and an energetically excited polaron. The quenching process is likely dependent on the spin state, which can be altered by spin mixing related to the zero-field splitting. In case quenching is not possible due to the spin configuration, the pair has to dissociate. The resultant polaron then remains trapped, whereas the triplet exciton can either decay or form a new triplet-polaron pair. In case the decay rate of triplet excitons is relatively small, it is most likely that...
triplet excitons sequentially form pairs with different trapped polarons until the right spin-configuration for quenching is obtained. In such a case, no high-field MFE in the current is expected. In the conditioned LEC discussed here the latter seems to be the case. One argument is the fact that singlet exciton quenching is already highly efficient in the doped regions, whereas the lifetime of singlets is typically a factor 10^3 smaller in MDMO-PPV than the lifetime of triplets. Furthermore, in a recent paper, Friend et al. characterized both triplet-triplet annihilation as well as triplet-charge quenching as the dominant triplet decay mechanisms in polymer LEDs.\textsuperscript{40} Therefore it is most likely that in the conditioned LEC no high-field MFE is observed. Another possible explanation for the absence of a high-field MFE is that the presence of ions favors spin mixing, suppressing effectively any magnetic field dependence of the transition between quartet and doublet states.

4. Magnetic field dependent triplet density: Effect on dielectric constant

An alternative explanation of MC in OLEDs was given in terms of a magnetic field dependent change in the dielectric constant $\varepsilon$.\textsuperscript{41} The recombination current is proportional to $\varepsilon$ via the Langevin factor $\lambda = q(\mu_n + \mu_p)/\varepsilon$. A change of 10% of $\varepsilon$ would then be necessary to explain the observed MC of $\approx \pm 10\%$. The change in $\varepsilon$ can originate from an altered triplet exciton density. The small dipoles formed by the triplet excitons are then expected to enhance the dielectric constant. If this would be the case here, then, in a hypothetical situation, a dramatic change of $\varepsilon$ far beyond 10% would be expected when comparing an unbiased device and a device biased at, e.g., 4 V. The difference in triplet density would be significantly larger than at $V < E_g$ with and without a magnetic field. Large changes in the dielectric constant in similar LECs biased at 0 and 4 V have, however, not been observed in impedance measurements.\textsuperscript{23} Hence we do not think that this alternative explanation is applicable to our results. On the contrary, we suggest that the effects observed in the air-treated MEH-PPV diodes in Ref. 41 can also be described by a triplet exciton dependent detrapping of polarons.

5. Device simulations

To check whether the proposed mechanism of triplet exciton assisted detrapping of polarons can explain the observed bias voltage dependence of the MC [see Fig. 2(d)], numerical drift-diffusion simulations were performed. The 1D drift-diffusion model presented earlier in this paper was used for this purpose. The model does not explicitly describe spin states or magnetic field effects. Nonetheless, these effects can be mimicked by altering parameters that are supposed to be magnetic field dependent.\textsuperscript{42} In Sec. IV D 3, the MC was attributed to an effective change in polaron mobility in the junction region. To model the effect of such a mobility change on the device current, the modeling results of the conditioned LEC shown in Figs. 6(a)–6(c) (straight lines) were used as starting points. Changing the polaron mobility in the complete device gives the trivial result of a proportional change in current. It was argued above, however, that only the mobility in the junction region is affected by interaction with triplet excitons. The carrier mobility in the junction region affects carrier transport as well as carrier recombination. Recombination is described by the Langevin description in the model and is proportional to the sum of the electron and hole mobilities: $R = \gamma n p$, where the Langevin factor is $\gamma = q(\mu_n + \mu_p)/\varepsilon$. Here, $n$ and $p$ are the respective electron and hole densities, $q$ is the elementary charge, $\mu_n$ and $\mu_p$ are the electron and hole mobilities, respectively, and $\varepsilon$ is the dielectric constant. To model the effect of an altered recombination rate due to a reduced carrier mobility, a prefactor $R_{\text{pre}}$ was introduced in the Langevin formula for the recombination rate: $R = R_{\text{pre}} \gamma n p$. A prefactor of 0.9 was used, mimicking a reduction of 10% of the carrier mobility in the junction region. The magnetococonductance was then determined by comparing the current for simulations with $R_{\text{pre}} = 0.9$ and 1.0. Similar modeling results were obtained when instead of changing $R_{\text{pre}}$, the electronic charge carrier mobility in the recombination zone was altered by 10% (see Fig. S7 in Ref. 20).

In Figs. 6(d) and 6(e), modeled $J-V$ and MC-V characteristics are shown in, respectively, a conditioned and a pristine device operating in steady state at different bias levels. In the conditioned device, the ions are artificially frozen at their positions after conditioning by setting the ion mobility to zero; in the pristine device, the ion mobility is nonzero, as this corresponds to a nonconditioned device. In the pristine device, no MFE in current is observed, whereas in the conditioned device, the decrease of the carrier mobility with magnetic field has resulted in a MFE in the current, denoted as MC = $(\text{MC} = \text{MC - gap} - \text{MC - gap})$ for $V_{\text{bias}} < E_{\text{gap}}$. Here, $I_{\text{MC - gap}}$ and $I_{\text{MC - gap}}$ represent the current for the cases when $R_{\text{pre}} = 0.9$ or 1.0. To make the modeling results resemble the experimental results at bias voltages around 0 V [e.g. Fig. 1(b)], a small, linear leakage current was added to the simulated current density. The leakage current dominates the total current at these relatively small bias voltages, leading to an effective reduction of MC. The small MC values around $V_{\text{bias}} = 0$ V may furthermore also be related to the relatively low generation rate of triplet excitons due to the low current density here.

For $V_{\text{bias}} > E_{\text{gap}}$, a positive MC is observed in Fig. 6(d) due to two artificial problems in the modeling. First of all, in reality the high bias voltage would enable the ions to move. The results in Fig. 6(e) show what the effect of mobile ions on the MC would be: $MC \approx 0$. Secondly, polaron detrapping in the junction region becomes less dominant: trap states are completely filled resulting in polarons to be in energetically higher-lying states, leading to a higher mobility. The current is therefore not dominated by traps anymore. As a result, the T-P effect is not likely to enhance the carrier mobility in this bias range: a change of 10% in electronic carrier mobility is most likely an overestimate. Therefore the part of the modeling for $V_{\text{bias}} > E_{\text{gap}}$ can be ignored.

The modeling results can be summarized as follows: a reduction of the carrier mobility in the recombination region can only reduce the total current through the device in the specific case that a fixed $p-i-n$ junction structure is present. This was achieved in the model by reducing the ion mobility to 0 during steady-state operation at $V_{\text{bias}} = 4$ V. For this, the applied bias voltage must be below the band gap of the semiconductor. In case $V_{\text{bias}} > E_{\text{gap}}$, the effect of the frozen $p-i-n$ junction is reduced due to the formation of electronic
space charge. Experimentally, the negative MC is measured at the same conditions as described here: a fixed p-i-n junction is present and electronic space charge is absent due to first conditioning the device at $V_{bias} = 4$ V followed by operation at $V_{bias} < E_{gap}$.

Considering all results together, we attribute the negative MC in conditioned LECs to polaron-triplet exciton interactions that lead to an enhanced carrier mobility in the trap-dominated intrinsic region. This effect is unique in LECs as opposed to OLEDs. In OLEDs, transport occurs by percolation through optimal pathways, which typically are not dominated by traps. In conditioned LECs biased at low-bias voltages, the trap density is large relative to the carrier density so that transport occurs from trap to trap. Interaction with triplet excitons can help to release carriers from these traps by transfer of energy from the triplet exciton to the trapped polaron. The observed magnetic field dependence itself does not originate from T-P interactions, but from the change in triplet exciton density. The triplet exciton density changes due to a change in singlet:triplet exciton formation ratio discussed in the previous section.

### E. High-field MFE in efficiency

The last observed MFE that has not been discussed yet is the effect in the efficiency that arises at $B_0 = 220$ mT and $V_{bias} > E_{gap}$ as shown in Fig. 2(d). The relatively large size of the characteristic magnetic field $B_0$ indicates a mechanism related to zero-field splitting. Furthermore, the effect only changes the electroluminescence, whereas it has no effect on the current. Species that may be involved because of their presence in the recombination zone are polarons and singlet and triplet excitons. Singlet excitons can interact with polarons leading to quenching. This quenching is, however, not magnetic field dependent. A possible MFE in the electroluminescence can originate from delayed fluorescence (DF) arising from triplet-triplet annihilation (TTA). 37,43,44

A pair of triplets can produce nine possible spin states with equal probability: a quintet, a triplet, and a singlet state. Due to spin conservation, only the latter can annihilate forming an excited and a ground-state singlet state. The excited singlet state can then relax by emitting a photon. This process is called delayed fluorescence (DF) and was recently shown to be of importance in OLEDs. 45 Mixing between all nine spin states is present and electronic space charge is absent due to first conditioning the device at $V_{bias} = 4$ V followed by operation at $V_{bias} < E_{gap}$.

Removal of the magnetic field then enhances this contribution at $V_{bias} = 4$ V to $\sim 17\%$. This means that a significant fraction of the electroluminescence in PPV-based LECs originates from DF by TTA.

### V. SUMMARY AND CONCLUSION

In summary, we have shown that light-emitting electrochemical cells can show large magnetic field effects because of trap-dominated transport and recombination in a relatively narrow region due to electrochemical doping. Large negative magnetoconductance values of around $\sim 12\%$ are observed in conditioned LECs simultaneously with a positive magnetoefficiency. Both effects originate from the competition between magnetic field dependent spin mixing and the formation rates of singlet and triplet excitons. The change in singlet:triplet ratio leads to the enhanced efficiency. The reduced triplet exciton density is suggested to lead to a reduction in polaron detrapping in the recombination zone, resulting in a reduced current density. At bias voltages that significantly exceed the semiconductor band gap, a negative magneto-electro-luminescence effect is observed arising at relatively large magnetic fields of 220 mT. This effect is attributed to delayed fluorescence, which originates from magnetic field dependent triplet-triplet annihilation. The contribution of delayed fluorescence to the total light output of the LEC is estimated to be at most 17\%.

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This means that 5 \times \frac{5}{18} \approx 17% of the singlet exciton density is due to DF from TTA in case no magnetic field is present.

One of nine possible spin states formed by two triplet excitons can generate one singlet exciton: 

$$1_{2S+1}L \rightarrow 1 S$$


