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F. L. Bloom,[a] W. Wagemans, M. Kemerink, and B. Koopmans
Department of Applied Physics, Center for NanoMaterials, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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In this work we examine the transition between positive and negative organic magnetoresistance in poly[2-methoxy-5-(3′, 7′-dimethyloctyloxy)-*p*-phenylenevinylene] in order to understand how different regimes of charge transport affect the organic magnetoresistance effect. To characterize the charge transport in these devices we measured the current, low frequency differential capacitance, and electroluminescence efficiency as a function of voltage. These measurements show that the sign change of the magnetoresistance corresponds with a change from a unipolar diffusive transport below the built in voltage (V_{bi}) to a regime of bipolar drift transport above V_{bi}. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3059555]

Organic magnetoresistance (OMAR) is a room temperature magnetoresistance that has been observed in *nonmagnetic* organic semiconductor materials contacted by nonmagnetic electrodes, which can be as large as 10% at fields of 10 mT.[1] It has been observed that the magnetic field can act to both increase the current, positive magnetoconductance ("+MC"), and decrease the current, negative magnetoconductance ("−MC"), depending on the device thickness[2] or the operating conditions, such as voltage[1,3] and temperature.[1,4]

The large magnitude at low magnetic fields, room temperature operation, and switchable sign of MC, not only makes these devices technologically interesting but also scientifically interesting since traditional magnetoresistance mechanisms fail to accommodate these properties. Recently, there have been several mechanisms proposed based on randomly oriented hydrogen hyperfine fields inducing spin mixing, which an external magnetic field acts to decrease. The spin mixing can induce singlet-triplet transitions of two-carrier states (i.e., excitons and bipolarons) or their precursor pairs. Bergeson *et al.*[5] proposed that this can increase e-h pair dissociation which can have a +MC or −MC depending on the transport regime. Hu and Wu[6] proposed that there is a competition between increased e-h pair dissociation, which only has a +MC in their model, and charge induced triplet-exciton dissociation, −MC. Desai *et al.*[2,7] explained OMAR as a competition between triplet-exciton polaron quenching, +MC, and triplet-exciton dissociation at interfaces, −MC. Finally, Bobbert *et al.*[8] explained that the change in the spin mixing can change the current by altering the process of bipolaron formation of electrons and holes separately which may have opposite signs.

It is clear from the models proposed above that understanding the sign change in OMAR is important for understanding its mechanism, and that these sign changes may be related to changes in the charge transport. Therefore, in this letter, we use current voltage $[I(V)]$, electroluminescence (EL), and low frequency differential capacitance (C) measurements to determine the correspondence between the charge transport and the sign of OMAR. We find that exactly at the voltage where the transport changes from a unipolar diffusive transport to bipolar drift transport there is a sign change from −MC to +MC. This behavior can be most plausibly explained using the bipolaron model.

We fabricated 3×3 mm^2 devices with the structure: glass/indium tin oxide (ITO)/PEDOT:PSS (60 nm)/MDMO-PPV (80 nm)/Ca (10 nm)/Al (100 nm), where PEDOT:PSS is poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), and MDMO-PPV is poly[2-methoxy-5-(3′, 7′-dimethyloctyloxy)-*p*-phenylenevinylene]. The polymer layers were fabricated by spin coating and after this step the samples were only exposed to an atmosphere of dry nitrogen. We also prepared samples with LiF (1 nm)/Al (100 nm) contacts which showed the same behavior as the Ca/Al sample presented here. MC and low frequency differential capacitance measurements were made between the poles of an electromagnet in the dark at room temperature. To prevent measuring changes in the current not due to magnetic field effects (e.g., time dependent drift of the current), we measured the MC using a lock-in amplifier to get the change in current induced by a small 27 Hz ac magnetic field on top of the dc magnetic field, resulting in $dI/dB(B)$. This is then integrated to obtain $[I(B)-I(0)]$ versus B.

First, we measured MC, given by $[I(B)-I(0)]/I(0)$, as a function of the magnetic field at several different voltages (Fig. 1). At low voltages the current decreases with increas-

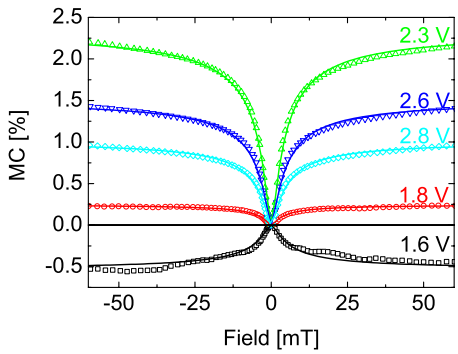

FIG. 1. (Color online) MC vs B for an ITO/PEDOT:PSS/MDMO-PPV (80 nm)/Ca/Al sample at several different voltages. The open symbols represent the measured data and the solid lines are fits to Eq. (1).

[a]Electronic mail: f.l.bloom@tue.nl.

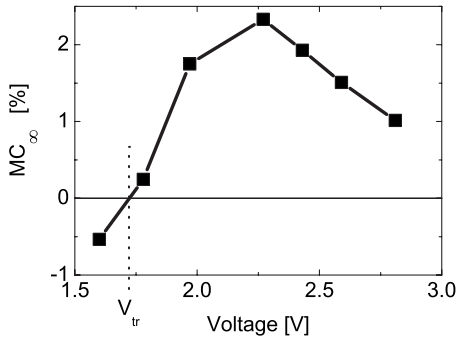

FIG. 2. MC_∞ vs voltage obtained from fitting Eq. (1) to the data in Fig. 1. The vertical dotted line represents the transition voltage (V_{tr}) from negative to positive MC.

ing magnetic field, resulting in a −MC. Increasing the voltage results in the MC changing sign, giving +MC. The MC(B) for both the +MC and −MC curves show good correspondence when fitted to (lines in Fig. 1),

$$\mathrm{MC}(B) = \mathrm{MC}_\infty \left[\frac{B}{(|B| + B_0)} \right]^2, \tag{1}$$

where B_0 is the characteristic field width and MC_∞ is the MC at infinite B-field.[1] Equation (1) was first found empirically[1] and later shown to be consistent with analytical[9] and numerical treatments[8] of the bipolaron model. From the resulting fits we observe that B_0 is larger for the −MC (3.0 mT) than for the +MC (2.0–2.3 mT), consistent with our previous work on Alq_3.[3] The most notable feature of the MC_∞ behavior is the sign change at 1.7 V, which is referred to as the transition voltage, V_{tr} (Fig. 2). As the voltage increases beyond the sign change, MC_∞ shows a sharp increase in magnitude which is followed by a slow decay. This behavior has also previously been observed in Alq_3 devices.[7]

To see if there are correlations between the sign of the MC and the charge transport we measured the current versus voltage [$I(V)$] characteristics [Fig. 3(a)]. From the $I(V)$ behavior we can see three distinct regions of charge transport. In the low voltage region (I) there is an Ohmic leakage current. At 1.2V there is an onset in the current which is the beginning of region II. In this region the current follows a power law dependence with a power law of V^n, with $n \sim 13$ [dashed line in Fig. 3(a)]. Region III begins at 1.7 V where the current increases with voltage faster than the power law dependence of region II. Understanding the transition between regions II and III is very important since the voltage at which it occurs ($V_{II \to III}$) is right at the voltage where the MC changes sign (i.e., $V_{II \to III} = V_{tr}$).

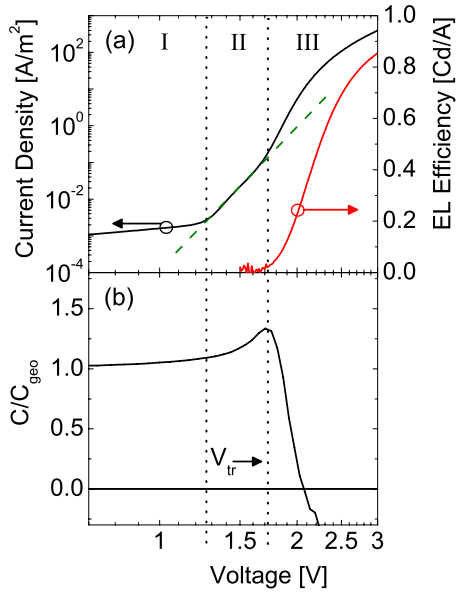

FIG. 3. (Color online) (a) log(I) (black), EL efficiency (red) and (b) low frequency (220 Hz) differential capacitance vs log(V). The dashed green line in (a) represents a power law fit to the log(I) vs log(V) in region II. The vertical dotted lines indicate the boundaries between regions I, II, and III.

Due to the good matching of the work functions of the ITO/PEDOT:PSS anode (5.1 eV) and the Ca cathode (2.9 eV) to the respective highest molecular orbital (5.3 eV) and lowest unoccupied molecular orbital (3.0 eV) of MDMO-PPV (Ref. 10) one would expect bipolar injection. By measuring the EL current efficiency [Fig. 3(a)] we can quantify how balanced the electron and hole populations are in the device. Interestingly, the EL current efficiency is ~0 below $V_{II \to III}$, indicating the current is likely to be highly unipolar in region II. At $V_{II \to III}$ bipolar injection begins and there is an onset in the EL efficiency indicating that in region III the device starts to become bipolar. This results in charges of opposites sign being introduced into the device, reducing the Coulomb repulsion and relaxing the space charge limitation of the current. Therefore, the current increases beyond the power law dependence in region II. The onset of EL efficiency at the deviation from the power law behavior confirms our previous assertion in Ref. 3 that this deviation is due to the device becoming bipolar. As the voltage increases further the EL efficiency increases, this is likely due to better charge injection at the minority charge (electron) injecting contact, Ca.

In this device, the difference between the work functions of the anode and cathode is 2.3 eV, which is close to V_{tr}. This suggests that the device is operating near the built-in voltage (V_{bi}). However, it is known that in organic devices injection barriers can vary by more than 1 eV from the vacuum level alignment at the interfaces.[11] Therefore, to accurately know (V_{bi}) it must be experimentally determined. We do so by utilizing low frequency differential capacitance measurements which detects the presence of diffused charge near the electrodes. Above V=0, carrier diffusion gradually increases causing the observed increase in C above the geometric capacitance (C_{geo}) [Fig. 3(b)], peaking just below V_{bi}.[12] Simultaneously, the diffusion current exceeds the leakage current increases as a power law which is in region II. As the voltage increases beyond $V_{II \to III}$, the transport goes from diffusion to drift, and correspondingly C decreases. As the voltage further increases in region III, C decreases below C_{geo} and even becomes negative as a result of the device becoming fully bipolar.[13]

From our results we can conclude that the transition from −MC in region II to +MC in region III occurs exactly at the transition from a dominantly unipolar diffusive transport regime to a bipolar drift regime. It is interesting that we can observe OMAR in the diffusive transport regime, and as far as we know this is the first observation of OMAR in this regime of transport. We have previously observed sign changes in Alq_3 where we saw similar correspondence of the $I(V)$ deviating from power law behavior and a sign change in the MC.[3] However, this transition occurred at voltages much

larger than V_{bi}. So it is likely that the change in the sign of the MC in the present case is due to a transition from unipolar to bipolar transport and not from a transition from diffusion to drift transport.

There are two different models that could show a sign change as the transport transitions from dominantly unipolar charge transport to bipolar transport. The work by Hu and Wu[6] proposes that there is a competition between triplet-charge reaction (−MC) and singlet e-h pair dissociation (+MC). According to the authors, when the charge transport in the device is unbalanced, the triplet-exciton charge reaction dominates due to the relatively long triplet-exciton lifetimes (note it is necessary for the device to be slightly bipolar in order to have enough triplet excitons to observe this effect). As the current becomes more balanced the singlet e-h pair dissociation becomes relatively more important and the MC changes sign. However, both the triplet-charge reaction and singlet e-h pair dissociation rely on the premise that the magnetic field can alter the singlet-triplet exciton ratio. This is not observed either in charge induced absorption[14] or fluorescence-phosphorescence measurements.[15] Also, it would be expected that if triplets played a role in the −MC, the −MC effect should have significant temperature dependence due to the strong dependence of temperature on the triplet lifetime. Experiments show that the −MC is only weakly affected by temperature.[4]

The other model that could explain this behavior is the bipolaron model. This model is based on unipolar charge transport and electron and hole mobilities can be separately effected by the magnetic field. Therefore, below V_{tr} the current is mostly unipolar and the majority carriers (holes) cause the MC. Above the transition voltage minority charge (electron) injection sets in and the minority charge carriers dominate the MC. It is possible for the minority charges to dominate the MC due to the compensation of space charge when the device becomes bipolar since the sum of the relative mobility changes in electrons and holes determines the MC.[3] So in MDMO-PPV where electrons have a significantly lower mobility than holes, electrons can still dominate the MC. Also, Nguyen *et al.*[16] showed in almost unipolar devices that the minority charge carrier conduction may dominate the MC. It has been shown in the bipolaron model that the sign of MC can be positive or negative.[8,9] However, in the bipolaron model, it is not obvious as to why in this device electrons give −MC and holes give +MC, while the opposite is true in Alq_3.[3] We note that our data are consistent with earlier observations that MC observed in the unipolar regime is generally smaller than that observed in the bipolar regime.[3] This trend is not yet understood, and provides an interesting challenge for future research.

In conclusion, we show by EL, $I(V)$, and low frequency differential capacitance measurements, that the voltage at which the sign change occurs shows remarkable correspondence with the transition from unipolar to bipolar transport, confirming our previous assertion.[3] The best existing model to explain this correlation seems to be the bipolaron model. However, the nature of how electrons and holes are affected differently within this framework remains an outstanding question.

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