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Frequency dependence of organic magnetoresistance

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To identify the microscopic mechanisms of organic magnetoresistance (OMAR), the dependency on the frequency of the applied magnetic field is explored, which consists of a dc and ac component. The measured magnetoconductance decreases when the frequency is increased. The decrease is stronger for lower voltages, which is shown to be linked to the presence of a negative capacitance, as measured with admittance spectroscopy. The negative capacitance disappears when the frequency becomes comparable to the inverse transit time of the minority carriers. These results are in agreement with recent interpretations that magnetic field effects on minority carrier mobility dominate OMAR. © 2010 American Institute of Physics. [doi:10.1063/1.3491217]

Organic magnetoresistance (OMAR) is a change in current on applying a magnetic field that is observed in a wide range of organic semiconductors.1 Because of its universal behavior and the observation of large effects (10%–20%) at relatively small fields and at room temperature, OMAR is both interesting for applications and from a scientific point of view. Several models have been proposed for OMAR,2–6 but the exact origin of the effect is still debated. In the models different mechanisms are suggested that affect processes in organic devices in different ways. These processes each occur on a different timescale. Therefore, performing measurements of OMAR on various timescales could provide clues about the processes relevant for OMAR, and thus discriminate between the proposed models. For instance, triplet (T) excitons could play a role in T–T annihilation or in reactions with charges,7 and these excitons have a typical lifetime of 25 μs.8 Traps have been suggested to enhance the magnetoconductance (MC), for instance via space charge effects9 and by conditioning the devices.10 Traps in the devices have a typical detrapping time from less than milliseconds up to hours, depending on how deep the traps are. Another typical timescale is the transit time, which is directly linked to the mobilities of the carriers, \( \tau = L^2/\mu V \), with \( L \) the device thickness, \( \mu \) the mobility, and \( V \) the voltage.1,11,12 Note that \( \tau \) is usually different for electrons and holes due to their different mobilities.

The frequency characteristics of OMAR have not been characterized before. In literature, only few experiments were reported in which the frequency of the applied magnetic field played a role. Veeraraghavan et al. reported no significant change in the response to an ac magnetic field for frequencies up to 100 kHz.13 On the other hand, a slow step response on the order of seconds was reported by Meruvia et al., which they suggested to be caused by the magnetic field acting on the trapping times.14 Finally, Majumdar et al. recently showed an increase in OMAR when the rate at which \( B \) was swept was decreased, which they conjecture could be caused by traps.15

In this Letter we show that OMAR is sensitive to the frequency of the ac component of the applied magnetic field. By comparing the frequency-dependent OMAR measurements with admittance spectroscopy, we relate the disappearance of OMAR to the transit times of the minority carriers. Finally, we discuss the consequences of these observations for the models suggested for OMAR.

We present experimental results on tris-(8-hydroxyquinoline) aluminum (Alq3)–based devices, but we note that we observed similar effects with PPV-based devices. The devices have the structure ITO/PEDOT: PSS(60 nm)/Alq3(100 nm)/LiF(1 nm)/Al(100 nm) and a 3×3 mm² junction area.16 Magnetic measurements were performed with an air coil through which a current with both a dc and ac component was sent. This resulted in a magnetic field \( B \) with an ac component with amplitude \( dB \). The ac response of the sample current \( dl \) was measured with a lock-in amplifier over a resistor in series with the sample, while a constant voltage was applied.10 Admittance spectroscopy measurements were performed with a Solartron SI 1260 impedance analyzer.

We measured the frequency dependence of the MC at different voltages, starting from a voltage just above the onset of OMAR. Plotted in Fig. 1(a) is the magnitude of \( L^{-1}dI/dB \) normalized at 1 Hz. \( dI/dB \) is the derivative of the current with respect to the magnetic field [inset Fig. 1(a)], which, when integrated, gives a typical OMAR curve.16 Here, however, we do not measure a full field sweep, but divide the signal at a fixed \( B \) by the current to get a measure for the MC: \( dMC/dB \). It was verified that the shape of the MC curves does not change with frequency, justifying this approach. To remove any extra signal from induction, picked up by the wires at higher frequencies, we measure the difference in signal at 2 and −2 mT, where \( dl/dB \) has an opposite sign.

For all measured voltages, the MC decreases with increasing frequency, see Fig. 1(a). At low voltages, the MC decreases faster than at higher voltages. The voltage dependence of the MC at fixed frequencies, extracted from Fig. 1(a), is shown in Fig. 1(b). At low frequencies, a typical MC(V) curve is obtained, which first increases with increasing voltage, has a maximum and then slowly decreases.16 For increasing frequency, the MC(V) curve collapses, with the strongest reduction at low voltages. Also plotted is the MC obtained from a quasi-dc measurement using a technique introduced in Ref. 16 (dashed line, right axis). This curve fits

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the extrapolation of the trend in the curves from 717 to 1 Hz, except for the two lowest voltages.

In addition to the response of the current to an ac magnetic field, we measured the response to an ac voltage, which is the admittance \( Y = dI/dV = G + i\omega C \), where \( G \) is the conductance, and the out-of-phase part is the angular frequency \( \omega = 2\pi f \) times the capacitance \( C \). In Fig. 2(a), below 7 V a decreasing capacitance as a function of frequency is observed, while for \( V \geq 7 \) V the capacitance starts negative and then converges to the low voltage signal. For increasing voltage, this negative contribution to the capacitance is more pronounced.

Interestingly, the absence of a negative contribution to the capacitance seems to be correlated with the suppression of the MC. We fit the frequency dependence of the MC with a stretched exponential, \( \tau_{\text{maj}} = \tau_{\text{maj}} \exp(-f/f_0)^{\alpha} \), where \( f_0 \) is a characteristic cut-off frequency and \( d = 0.46 \) is a stretching parameter that is kept the same for all curves [lines in Fig. 1(a)]. In Fig. 3, both \( f_0 \) and the frequencies where the capacitance is 95% of its low voltage value, \( f_C \), are plotted as a function of voltage. A clear correlation between the two frequencies is observed and both curves are approximately showing an exponential increase with voltage. We verified that the equivalent circuit of the sample and series resistor shows no frequency dependence in the range studied.

In order to interpret the correlation between \( f_0 \) and \( f_C \), first, we will discuss the observed trends in \( C \). In Fig. 2(b) frequency dependencies of a prototype single-carrier and double-carrier device are shown, simulated using an approach similar to Ref. 17. In a single-carrier device, at \( f > 1/\tau_{\text{maj}} \) the dielectric properties of the organic material are probed, giving the geometric capacitance \( C_{\text{geo}} \). At \( f \ll 1/\tau_{\text{maj}} \) the (majority) charges in the device easily follow the voltage modulation and due to charge relaxation \( C = 3/4C_{\text{geo}} \). The transition between these two regimes occurs around \( f = 1/\tau_{\text{maj}} \). Traps increase the ability of the device to store charges, resulting in an increased capacitance, which decreases as the frequency becomes larger than the inverse trapping time, eliminating the contribution from the traps [Fig. 2(b), dotted line]. In a double-carrier device, due to cancellation of the space charge, a much larger amount of charge can be stored, resulting in a large capacitance, which,

FIG. 1. (Color online) (a) \( MC/\Delta B \), normalized at 1 Hz, as a function of frequency for different voltages, using \( \Delta B = 0.5 \) mT. The lines are a fit to a stretched exponential. Inset: \( dI/dV \) at 10 V, 120 Hz, corrected for offset. (b) \( MC/\Delta B \) as a function of voltage for different frequencies (left axis) and MC as a function of voltage for \( B = 83 \) mT, measured with a permanent magnet (small symbols, right axis), see Ref. 16.

FIG. 2. (Color online) (a) Capacitance as a function of frequency of the ac voltage (50 mV) for different dc voltages. \( f_0 \) is defined where \( C \geq 95\% \) of the low voltage value, as 100% is less defined. (b) Simulation of the capacitance of a single-carrier device with (dotted line) and without (dashed line) traps, and of a double-carrier device (solid line). Frequency scaled with transit time \( \tau \) of majority carriers (\( \mu_{\text{maj}} = 0.01 \mu_{\text{maj}} \)).

FIG. 3. (Color online) Characteristic frequencies \( f_0 \), from fitting Fig. 1(a), and \( f_C \), from Fig. 2(b), as a function of voltage.
due to a lag in signal, is negative. Above $1/\tau_{\text{min}}$ of the slowest (minority) carriers, the capacitance starts to follows the single-carrier case.\textsuperscript{11,12}

Now, we can interpret the measured capacitance as shown in Fig. 2(a). For $V \leq 6$ V the device is single carrier and contains traps, while, starting from 6 to 7 V, minority carriers (holes) are injected as is evident from the presence of a negative capacitance at low frequencies. The contribution of the minority carriers is present up to increasing frequencies for increasing voltage reflecting the decrease in $\tau_{\text{min}}$ as can be seen from the voltage dependence of $f_C$ in Fig. 3.

Therefore, the correlation between $f_0$ and $f_C$ implies that the MC is significantly reduced beyond frequencies where the ac response of the minority carriers is diminished. Next, we will sketch the implication of this conclusion for the different models, but we first note that a correlation between a voltage modulation and magnetic field modulation is not trivial. With a voltage modulation the electric field is changed, $E(t)$, while a change of the magnetic field changes the mobility or recombination mobility, $\mu(B(t))$. For a single-carrier device, a change in $E$ requires a change in the charge distribution in the device, while only a change in $\mu$ does not. In a double-carrier device a more complex situation is expected as injection and recombination also affect the charge distribution in the device.

A magnetic field variation can affect the mobility, but also the reaction between electrons and holes, influencing the recombination mobility through the recombination probability. In the bipolaron model, the magnetic field acts on the electron and/or hole mobility,\textsuperscript{3} while in the electron-hole model,\textsuperscript{2} the recombination mobility is believed to be changed. On the experimental timescales, fast processes like individual recombination or hopping events are not limiting. To qualitatively get an idea about the effect of a reduction in the contribution of minority carriers, we will discuss three different scenarios: the magnetic field acting on the recombination mobility, the majority mobility, or the minority mobility.

First, let’s consider the scenarios where the magnetic field acts only on the majority mobility ($d\mu_{\text{maj}}/dB \neq 0$) or the recombination mobility ($d\mu_r/DB \neq 0$). In a double-carrier device with recombination, if any of these two mobilities changes, the charge balance in the device will change, requiring charges to be injected or extracted. The frequency dependence of this injection and extraction is described by the admittance. At low frequencies, both minority and majority carriers can respond to the change in mobility $\mu_{\text{maj}}$ or $\mu_r$, canceling each others space charge and thus allowing large changes in charge density and consequently in current (hence, also a large negative capacitance is observed). At higher frequencies, where the minority carriers can no longer keep up with the change, only the majority carriers will respond. Now, the minority carriers cannot optimally compensate the resulting space charge, giving a much smaller, but finite, response in the current and thus the observed MC. Note that even while $d\mu_{\text{min}}/DB = 0$ in these two scenarios, $\mu_{\text{min}}$ still plays a crucial role in setting magnitude and timescale of the response.

Finally, in the case of the magnetic field only acting on the mobility of the minority carriers ($d\mu_{\text{min}}/DB \neq 0$) a similar argument as above also results in a decrease in MC with increasing frequency. However, the change in the current is going to zero at high frequencies. This interpretation is in agreement with recent experiments on OMAR in single carrier devices in which it is shown that the magnetic field acts most strongly on the minority carriers.\textsuperscript{6} Moreover, it has been shown that even in double-carrier devices, the magnetic field effects in the minority mobility dominate the total magnetic response of the current, even though the majority mobility is much larger.\textsuperscript{9,19}

All three scenarios are thus capable of explaining the correlation between $f_0$ and $f_C$. However, although a good qualitative explanation of the observed effects is given, other origins or more complex interactions cannot be excluded. While we unambiguously demonstrated the role of the minority carriers, a more refined conclusion could be drawn only after performing detailed device simulations. Such an effort should also take into account effects due to traps and injection barriers, and is considered to be beyond the scope of our present letter.

In conclusion, we have shown frequency dependent OMAR measurements, using a superposition of a dc and an ac magnetic field. We observed a decrease in MC with increasing frequency. The decrease is stronger for lower voltages, which is shown to be linked to the presence of a negative capacitance that disappears when the frequency becomes comparable to the inverse transit time of the minority carriers. We showed that this interpretation is in agreement with recent experiments. However, device simulations need to be performed to discriminate between different models.

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\textsuperscript{7}B. Hu, L. Yan, and M. Shao, Adv. Mater. 21, 1500 (2009).


