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Influence of trap sites on organic magnetoresistance

Wijnen, M.H.A.

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Influence of trap sites on Organic Magnetoresistance

Wijnen, M.H.A.

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Organic semiconductors are making their way into modern electronics, and are used in devices such as organic light emitting diodes (OLEDs). A novel effect in these materials is organic magnetoresistance (OMAR). Applying a small field (of approximately 10 mT), can lead to changes in the order of 10% in the conductance and light emission of a device. These changes are called magnetoconductance (MC), and magneto-electroluminescence (MEL) respectively. Research in this field can lead to more insight in the fundamentals of organic devices, and to the discovery of new applications. Recent discoveries suggest that so called traps are very important to these magnetic field effects (MFEs). These traps are imperfections in the device with a narrower band gap, that can capture electrons or holes.

This project investigates the role of different kinds of traps on MFEs in a blue polymer OLED. First, we create traps by incorporating different molecules, called dyes, into the host polymer. Two dyes are used, that emit green and red light respectively. Next, traps are created by electrical conditioning, i.e. 'damaging' the device by a large electric current. It is investigated how these traps influence the MC, MEL and magnetic field dependence of the luminescence spectrum. The last method provides a new way to investigate the effect of traps. It can distinguish between the MEL of the traps themselves, and their influence on the rest of the polymer (backbone).

We found that the green dyes were unable to act as traps, but the red were. The latter were found to have a positive MEL, but they significantly reduced the MC and MEL of the backbone. The exact opposite was observed with the traps caused by conditioning. Surprisingly, both types of traps could strongly influence the magnetic field dependence of light emission from the backbone. None of the existing theories of OMAR was able to explain these results. Therefore, a new model was developed, which is based on the formation of triplet excitons at trap sites. It can explain why, under a magnetic field, the traps emit less light and the backbone more, or vice versa. With a few simple assumptions, it was able to explain the experimental results, as well as several findings in the literature. Numerical simulations based on the model could predict the voltage dependence of the MFEs, which agreed with observations in many devices.

Our experiments have shown that trap sites do indeed play a very important role in MFEs in organic materials. However, the underlying mechanism proved to be different than thought before. We have shown the importance of physics at the macroscopic level and developed a new model explaining various observations.
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Chapter 1

Introduction

Organic semiconductors are quickly getting more important in modern electronics. Promising applications are flexible displays and cheap plastic solar cells. Currently, organic (OLED) displays are already available in mobile phones and televisions. Organic materials mainly consist of the elements carbon and hydrogen. They form the basis of all living organisms, but also of synthetic materials such as plastics. An important class of organic materials are polymers, molecules consisting of long chains of carbon atoms. Organic materials were well known for their insulating properties, until in 1977 Shirakawa et al. discovered that some polymers can conduct electricity. Their discovery has led to the development of many new technologies such as organic light emitting diodes (OLEDs), and has been awarded with the Nobel Prize in chemistry in 2000.

Organic materials are not magnetic and for long it was thought they would not respond to magnetic fields. However, in 2004 Francis et al. discovered an effect called organic magnetoresistance (OMAR) [1]. Applying a small magnetic field of just a few mT to an OLED device results in a change of up to 10% in the electric current and/or light emission. The effect is present in virtually all organic semiconductors. Therefore it is thought to be intrinsic to these materials and interesting from a fundamental point of view. Research on OMAR can lead to the development of new magnetic devices, but also provides a better understanding of organic semiconductors in general.

The exact origin of OMAR is currently still under debate in the scientific community. Several models have been proposed, that explain OMAR in different devices under different circumstances. All of these models share one common mechanism: the interaction between the spins of particles present in an organic device. Applying an external magnetic field influences this interaction. Each model relies on different particles, such as electrons, holes, and excitons, which are quasi-particles formed from electron-hole pairs.

Recent research suggests that so-called trap sites are very important to the origin of OMAR. These traps are imperfections in the organic semiconductor that can capture free electrons or holes. These particles become immobile and can therefore not contribute to electrical conduction. Traps can be created by damaging the device, e.g. by high electric currents or radiation exposure. Experiments show that increasing the amount of trap sites can greatly enhance OMAR [2]. Based such experiments, Cox et al. have proposed a new model in which
traps play an important role [3]. At these sites, metastable particles called trions are formed out of triplet excitons and free charges. This process is dependent on the magnetic field and can explain the OMAR effect.

A completely different use of traps is to alter the light emission of an OLED device. Because traps have a narrower band gap than the rest of the material, they emit light of less energy and a longer wavelength. Nicolai et al. have incorporated traps that emit red and green light into a blue light-emitting polymer to create a white OLED [4]. These traps were created by incorporating dyes, chemical compounds with a different band gap, into the host polymer. In this way, the properties of a device can be precisely controlled by manipulating the chemical properties and concentrations of the dyes.

**This project**

During this project, the effects of these chemically engineered traps on OMAR are investigated. Unlike traps created by damage to the device, these might provide a more controllable way to manipulate the magnetic properties of an organic semiconductor. Devices are characterized by their magnetoconductance (MC) and magneto-electroluminescence (MEL). These are the respective changes in conduction and luminous efficiency when applying a magnetic field. Also, we investigate how the emission spectrum of a device changes when applying a magnetic field. This provides a new method to investigate the influence of traps, because it is possible to observe the energetic transitions at the traps and at the rest of the polymer separately. In the same backbone polymer, traps are also created by electrical conditioning, i.e. sending a high current through the device. These traps are investigated using the same methods. The results from both traps are compared with each other, and with the current theoretical models. Also, a new device model will be developed.
Chapter 2

Theory

This chapter will provide a short theoretical background in organic spintronics. The first section will cover the basics of electrical conductance in organic materials. The second section will discuss magnetic field effects in these materials and will shortly explain several recent models for these effects.

2.1 Organic semiconductors

2.1.1 $\pi$-Conjugated molecules

Conduction in organic materials is possible due to $\pi$-conjugation. This effect occurs on the carbon chain of an organic molecule and is usually described by alternating single and double bonds. A simple example is polyacetylene, depicted in Figure 2.1. The carbon atoms each have three $sp_2$ and one $p_z$ orbital. The $sp_2$ orbitals lie in the plane of the molecule and overlap to form strong $\sigma$-bonds with adjacent carbon and hydrogen atoms.

The $p_z$ orbital overlaps with neighbouring $p_z$ orbitals to form $\pi$-bonds. The $\pi$-electrons are delocalized along the molecule, which causes the conductive properties. For each $\pi$-bond there are two possible states, bonding and anti-bonding. The delocalized electrons occupy the bonding states, while the anti-bonding states remain empty. Due to Peierls distortion, delocalization does not spread over the entire molecule, but alternating single and double

![Figure 2.1](image)

*Figure 2.1: (a) Structure of polyacetylene. (b) Schematic picture of polyacetylene showing the $\sigma$- and $\pi$-bonds. Figure obtained from [5]*
bonds are formed. This causes the energy of the antibonding states to increase with respect to the bonding states. This energy gap leads to semiconducting behaviour.

The bonding orbital with the highest energy is called Highest Occupied Molecular Orbital (HOMO) and the antibonding orbital with the lowest energy is called Lowest Unoccupied Molecular Orbital (LUMO). These are comparable to the valence and conduction bands in inorganic semiconductors.

2.1.2 Charge conduction

The structure of organic materials is highly disordered due to irregular deposition of molecules and structural distortion in polymer chains. This disorder causes charges to be localized on single molecules, or parts of the molecule. The energy levels of these sites are also disordered and can be described by a Gaussian density of states with a width of $\sigma \approx 75 - 150\text{meV}$ [6]. Charges can move from one site to another via a mechanism called hopping, which is based on phonon-assisted tunnelling. The rate of hopping between states is given by [7]:

\[
n_{\text{hop}} = \nu_0 \exp(-2\alpha R) \begin{cases} 
\exp\left(-\frac{\Delta E}{k_BT}\right), & \text{for } \Delta E > 0, \\
1, & \text{for } \Delta E \leq 0,
\end{cases}
\]

with $\nu_0$ the hopping attempt frequency, $\alpha$ the inverse localization length, $R$ the distance between the sites, $\Delta E$ the energy difference and $k_BT$ the thermal energy. This equation expresses a trade-off between hopping distance and energy difference. Applying an electric field leads to an energy gradient and therefore a preferential direction for hops to occur, resulting in an electric current. The hopping character greatly reduces charge mobility compared to inorganic semiconductors.

2.1.3 Electric current

A typical organic device consists of the active organic layer sandwiched between two (metal) electrodes. When a voltage is applied, charges are injected from the electrodes and conduction occurs. In this study, bipolar devices are used in which both electrons and holes contribute to conduction. Electrons are injected at the negative electrode (anode), and holes at the positive electrode (cathode). The presence of an electron or hole induces a distortion in the environment. The charge and distortion together can be treated as a quasi-particle, called a polaron. For the sake of simplicity these polarons are referred to as electrons and holes throughout this report.

Figure 2.2 shows the energy diagram of a simple organic device. The organic layer is placed between a hole and an electron injection electrode with work functions $\Phi_h$ and $\Phi_e$ respectively. No bias voltage is applied, therefore the Fermi levels of the electrodes are aligned. To enable charge injection, the work functions of the positive and negative electrodes need to match the HOMO and LUMO respectively. To obtain currents in the device, the bias voltage needs to overcome the built-in voltage $V_{bi}$ of the device, which is the difference between the electrode work functions.
When the bias voltage is below $V_{bi}$ conduction is still possible. In this case the device will act as a diode and the current density is described by the Shockley diode equation [9]:

$$J = J_s \left( \exp \left( \frac{qV}{k_B T \eta} \right) - 1 \right),$$

(2.2)

with $J_s$ the saturation current density at negative bias, $\eta$ the ideality factor and $q$ the elementary charge.

In a real device an energy mismatch called the injection barrier exists between the electrodes and the HOMO and LUMO of the organic semiconductor. $\phi_h$ and $\phi_e$ are the injection barriers at the hole and electron injection electrodes respectively. When the bias voltage is just above the injection barrier, charge injection is possible due to tunnelling and thermal assistance. Current is limited by the ability of charges to overcome this barrier, therefore it is called injection limited current (ILC).

At higher voltages current is no longer limited by the injection of charges, but by the ability of charges to move to the opposite electrode. The resulting current is called space charge limited current (SCLC) because it is hindered by the accumulation of charges in the device. In this regime the current density is given by the Mott-Gurney equation [10]:

$$J = \frac{9}{8} \mu \epsilon \frac{(V - V_{bi})^2}{L^3},$$

(2.3)

where $\mu$ is the mobility of the relevant charge carrier, $\epsilon$ the electric permittivity and $L$ the device thickness. In the case of a bipolar device, where both electrons and holes contribute to the conduction, SCLC is given by:

$$J = \frac{9}{8} \epsilon \sqrt{\frac{2\pi \mu_e \mu_h (\mu_e + \mu_h)}{\mu_r}} \frac{(V - V_{bi})^2}{L^3},$$

(2.4)
where $\mu_h$, $\mu_e$ and $\mu_r$ are the hole, electron and recombination mobilities. In this case, net charge is cancelled by the presence of both electrons and holes. This allows more charge carriers at the same place and thus higher current densities. On the other hand, electrons and holes can also recombine, reducing the current because charges do not reach the opposite electrode.

2.1.4 Trap sites

Traps are sites with an energy level that lies within the band gap of the semiconductor, and thus are able to trap charge carriers, see Figure 2.3. These states commonly occur due to defects or impurities, but also at the tail of the density of states of the HOMO and LUMO. Charge mobility is reduced by the presence of traps, because charges can stay at these sites for very long times before being (thermally) released. Applying a higher bias voltage tilts the energy landscape and can release charges from traps, making them contribute to conduction again. Traps influence current characteristics, leading to a SCLC density that scales as

$$J \propto \frac{(V - V_{bi})^{n+1}}{L^{2n+1}},$$

with $n > 1$ [11]. Traps can be artificially created by introducing dopant molecules in the semiconductor [12], or by copolymerization of a molecule with a lower band-gap into the host polymer [4]. During this internship the latter method will be used to influence magnetic field dependent properties of organic materials.

![Figure 2.3: Schematic drawing of an electron trap, with its energy level below the LUMO. An electron can move through the material by means of hopping, and fall into the trap.](image)

Trap sites have an important influence on electron-hole recombination processes. On the host polymer, recombination occurs according to the Langevin mechanism. The rate of this process is determined by diffusion of electrons and holes toward each other. The recombination rate is given by [13]:

$$R_L = \frac{q}{\epsilon} (\mu_h + \mu_e) np,$$

where $n$ and $p$ are the electron and hole densities.

Traps can assist recombination, which was first described by Shockley, Read, and Hall in 1952 [14, 15]. This process consists of two steps. First a charge is captured at a trap site, where it can stay for a relatively long amount of time. Charges of opposite sign can diffuse toward
the site and recombine with the trapped particle. In OLEDs, where the electron and hole densities are assumed equal and electrons the particles being trapped, the SRH recombination rate is given by [13]:

$$R_{SRH} = \frac{q}{\epsilon} \mu_h N_t p,$$

where $N_t$ is the trap density.

The recombination process is usually radiative, i.e. a photon will be emitted. Because traps have a narrower band-gap, light emitted at these sites will be of a longer wavelength. Therefore they can be utilized as dyes to change the color properties of these polymers. For example, red and green dyes can be incorporated in a blue light-emitting host polymer to create a white OLED [4].

A notable difference between these processes is that the Langevin recombination rate is quadratic in charge carrier density, whereas SRH is linear. This means that the ratio $R_{SRH}/R_L$ will decrease with charge density and thus with voltage. Because emission at trap sites is of a longer wavelength, this results in a relative decrease of the long wavelength components in the spectrum.

A different mechanism for recombination at a dye is Förster resonance energy transfer (FRET) [16]. In this case recombination occurs on the host polymer according to the Langevin mechanism. However, no light is emitted. Instead, the energy is transferred via a non-radiative process to a dye molecule, that becomes excited. When the dye falls back to the ground state, it will emit a photon with the energy of its own band-gap, which is generally lower than that of the host polymer. Because recombination takes place on the host polymer, the rate at which it occurs is proportional to $R_L$ in (2.6). Contrary to the SRH mechanism, the ratio between luminescence on the dyes and the host polymer is independent of voltage. One requirement for FRET to occur is spectral overlap between the donor (backbone) and acceptor (dye) molecules.

During this project the effect of traps on magnetic field effects is investigated by incorporation of green and red dyes in a blue backbone polymer. The same copolymers have also been investigated by Nicolai et al. [4]. It was found that the luminescence at the green dye is caused by energy transfer from the backbone, while luminescence at the red dye can be attributed to SRH recombination.

### 2.2 Magnetic field effects

Organic magnetoresistance is a change in current through an organic device when a magnetic field is applied. The observed effects are strong and occur at room temperature and magnetic fields in the mT range. OMAR is characterized by magnetoconductance, the relative change in current when a magnetic field is applied, which is given by:

$$MC(B) = \frac{I(B) - I(0)}{I(0)},$$

where $I$ is the current at a constant bias voltage, and $B$ the applied magnetic field.
In organic light-emitting diodes (OLEDs) not only current but also electroluminescence can be influenced by a magnetic field. The effect is described by magneto-electroluminescence, which is defined as:

\[
\text{MEL}(B) = \frac{\text{EL}(B) - \text{EL}(0)}{\text{EL}(0)},
\]

where \(\text{EL}\) is the amount of electroluminescence. Luminescence is dependent on current density, therefore a change in current by a magnetic field would automatically lead to a change in luminescence. However, a change can be observed even if the current is kept constant. It is this change that is referred to as the MEL, which can therefore be seen as a change in luminous efficiency.

![Graphs showing different magnetic field effects](image)

Figure 2.4: Examples of different magnetic field effects. (a) A positive and negative low-field effect. (b) Low-field effect combined with a high-field effect. (c) The ultra small field effect. Figure obtained from Wouters [17]

A typical example of an MC\((B)\) curve is shown in Figure 2.4a. The shape can be described by a Lorenzian curve. This function is predicted by theories of classical magnetoresistance and is given by [18]:

\[
\text{MC}(B) = \text{MC}_{\infty} \frac{B^2}{B^2 + B_0^2},
\]

where \(\text{MC}_{\infty}\) is the magnetoconductance at infinite magnetic field and \(B_0\) the half-width at half-maximum. These parameters give insight about the magnitude of the effect and at which field scales it occurs. However, this function does not always apply well to observed lineshapes. A so called non-Lorenzian has been proposed that fits better to empirical data:

\[
\text{MC}(B) = \text{MC}_{\infty} \frac{B^2}{(|B| + B_0)^2},
\]

Sometimes an additional effect can be observed at high field intensities, as shown in Figure 2.4b. The resulting lineshape can be fitted with a double non-Lorenzian function:

\[
\text{MC}(B) = \text{MC}_{\text{LFE}} \frac{B^2}{(|B| + B_{\text{LFE}})^2} + \text{MC}_{\text{HFE}} \frac{B^2}{(|B| + B_{\text{HFE}})^2},
\]

where \(\text{MC}_{\text{LFE}}\) and \(B_{\text{LFE}}\) describe the low-field effects, and \(\text{MC}_{\text{HFE}}\) and \(B_{\text{HFE}}\) the effects at high fields.
The same relations can be used to describe MEL\((B)\) curves. In some cases, even more complicated behaviour is observed, such as the ultra small field effect shown in Figure 2.4c.

2.2.1 Models

Several mechanisms have recently been proposed to explain the origin of organic magnetoresistance. Different models exist for different types of devices and magnetic field regimes. However, debate is still going on about the exact mechanism, and none of the current models can completely explain all the observed magnetic field effects. Still, all contemporary models are based on a common principle: the interaction between the spins of electrons and holes, and magnetic fields.

Charged particles, such as electrons and holes, interact with the nuclei of hydrogen atoms attached to the backbone of the polymer chain through hyperfine interaction. This interaction can be described as precession of the spin of the particle around a magnetic field. This magnetic field is the sum of the fields induced by the nuclei of different hydrogen atoms. This field has a random orientation and is different at different sites, as shown in Figure 2.5a. At these sites two polarons are drawn that are initially in a triplet configuration with parallel spin (solid arrows). By precessing, their configuration can change into a singlet state. (dashed arrows). When an external magnetic field is present, spins will precess around the total magnetic field, as shown in Figure 2.5b. It is now less likely that two spins can change between singlet and triplet states. This suppression of spin mixing lies at the origin of the models described here.

**Electron-hole pairs**

One of the models explaining OMAR is the electron-hole pair model, proposed by Prigodin
et al. in 2006 [19]. It is applicable to devices in which both electrons and hole are present. The model is based on interactions between these particles, which are illustrated in Figure 2.6. When electrons and holes approach each other, they can form a bound pair due to Coulomb attraction. Pairs are formed in singlet (S, spin 0) and triplet (T, spin 1) states, with a statistical ratio of 1:3. Because the charges still reside on different parts of a molecule, these states can be mixed by hyperfine fields.

Pairs can either dissociate into free charges, or approach each other until their wave functions overlap. This state is called an exciton, and is basically an excited state of a molecule. Pri-godin et al. assumed that the exciton formation rate for triplets ($k_T$) is higher than that of singlets ($k_S$). Due to this difference, many pairs that start in a singlet state will mix into a triplet configuration and form a triplet exciton, indicated by the dashed path in Figure 2.6. Therefore, the ratio of singlet:triplet excitons will be lower than 1:3.

The formation of excitons reduces the amount of charge carriers in the device and therefore lowers the current. Applying a magnetic field suppresses hyperfine mixing and blocks the dashed path in Figure 2.6. This decreases the formation of (triplet) excitons and allows more pairs to dissociate, leading to a higher current. Thus the electron-hole mechanism leads to a positive MC. The typical magnetic field scale at which this effect occurs is that of the hyperfine field, $1 - 10 \text{mT}$.

It must be noted that singlet excitons will recombine by emitting a photon, while this process is spin forbidden in the case of triplet excitons. Triplets can still recombine, but through non-radiative processes that take place at much longer timescales. Applying a magnetic field will increase the amount of singlet pairs, and thus the formation and recombination of singlet excitons. This will lead to increased light emission. The e-h pair mechanism therefore results in a positive MEL, as reported in the literature. This validates the assumption made previously that $k_T > k_S$.

Several other mechanisms exist that explain certain OMAR effects. One of these is the bipolaron mechanism proposed by Bobbert et al. in 2007 [20]. It shares similarities to
the mechanism discussed above except that it regards interactions between equally charged polarons. It is mainly applicable to unipolar devices and leads to negative MC.

2.2.2 Exciton-charge mechanisms

The electron-hole pair mechanism provides a qualitative explanation of OMAR. However, it requires that pairs have a high chance of dissociating into free charge carriers. This is unlikely due to their high binding energy (1 eV) compared to the thermal energy at room temperature ($\approx 25$ meV).

A different mechanism was proposed by Desai et al. [21, 22], which is based on the interactions between triplet excitons and charges. Because triplet excitons have a much larger lifetime than singlets, it is expected that large concentrations of triplet excitons are present in organic devices. It is therefore likely that these excitons interact with other charges.

One possible interaction is the scattering of a free charge carrier by an exciton. This reduces the charge mobility, decreasing the current. As explained previously, applying a magnetic field reduces the triplet concentration and thus scattering of charges. This mechanism therefore leads to a positive MC at low magnetic fields.

Another possible mechanism is that a triplet exciton recombines to the ground state upon reacting with a separate charge. The energy of that charge is increased and its spin is flipped, to conserve total spin. If trapped, the charge would be de-trapped by the extra energy which leads to an increase in current. This reaction is magnetic-field dependent and is suppressed at high magnetic fields [23], therefore leading to a negative high-field MC.

Trion mechanism

Recently Cox et al. [3] proposed a new mechanism, referred to as the trion mechanism, that is also based on triplet exciton-charge interactions. It is suggested that these excitons can capture charges and thereby limit the current. Kadashchuk et al. [24] have shown that these excitons and charges can form metastable particles called trions if formed at trap sites. These trions have lifetimes in the order of milliseconds. Because they are immobile and have very long lifetimes, trions hinder the current significantly and are therefore regarded as a possible origin of OMAR.

Due to electron-hole interactions, applying a magnetic field reduces the amount of triplet excitons. Therefore less trions are present that can hinder the current. The result is a positive low-field MC, similar to that of the triplet-exciton mechanism by Desai et al.

Charges and excitons approaching each other form pairs before combining into a trion. The spin state of these pairs is either a doublet (D, spin $\frac{1}{2}$) or quartet (Q, spin $\frac{3}{2}$) configuration. Spin mixing occurs between these states and is suppressed at a high magnetic field scale, related to zero field splitting of the triplet exciton. This mixing effect can be used to explain the high field effects in the MC.

One of the advantages of the trion mechanism is that an analytical expression can be derived that correctly explains the voltage dependence of the MC. The expression can be derived
from the rate equations that describe the formation of trapped electrons, triplet excitons and quartet trions. Parameters used in the model are the trap density \( N_t \), the coefficients for electron trapping \( \gamma_t \), recombination \( \gamma_R \), and triplet-polaron interaction \( \gamma_{TP} \). Furthermore \( P_T \) and \( P_Q \) are the magnetic field dependent formation probabilities of triplets and quartets, and \( k_T \) and \( k_Q \) their respective recombination rates. The equation for the MC is given by:

\[
MC(p) \approx \Delta P_T C p \frac{k_T + 2\gamma_{TP} p}{(b_0 + b_1 p + b_2 p^2)^2},
\]

where \( C = k_Q P_Q N_t (\gamma_t + \gamma_R) \), \( b_0 = k_T k_Q (\gamma_t + \gamma_R) \), \( b_1 = k_Q (P_T \gamma_t \gamma_R + 2\gamma_{TP} (\gamma_t + \gamma_R)) \) and \( b_2 = 2P_T P_Q \gamma_t \gamma_R \gamma_{TP} \). Finally, the relation between the hole density \( p \) and voltage is needed. Cox et al. use the SCLC relation (2.4) and the drift equation \( J \approx \mu_h p q (V - V_{bi})/L \) to find the following linear relation:

\[
p = \frac{9\epsilon}{8qL} \left( 1 + \frac{\mu_e}{\mu_h} \right)^{-1} \sqrt{\frac{2\pi \mu_e}{\mu_h}} (V - V_{bi}) = a(V - V_{bi}).
\]

With this relation \( MC(V) \) can be found.

Figure 2.7 shows the typical voltage dependence of the MC predicted by Eq. (2.13). At voltages near \( V_{bi} \) the MC increases rapidly, which be explained by the increasing formation of trions. This process is trap-assisted and scales linearly with \( V - V_{bi} \). At high voltages, the MC drops with \( (V - V_{bi})^{-2} \). This can be explained by the fact that all traps are filled and no extra trions are formed with increasing voltage. The density of free polarons still rises, thereby decreasing the relative effect of the trions.

Equation (2.13) predicts that the MC increases with the trap density. During this project it is investigated if adding different types of traps can indeed enhance the MC.

2.2.3 Degradation

A well known problem of organic electronics is that these materials are prone to degradation. Devices are damaged by external influences, such as exposure to oxygen and water, or UV and X-ray radiation. Intrinsically degradation also occurs when current flows through the device. These effects commonly reduce device performance, i.e. conductance and luminous efficiency. Still, the underlying mechanisms are not exactly known. Possible defects that might
be formed are, amongst others, chemical changes, breaking of polymer chains, cross-linking and morphological changes.

In blue polyfluorene OLEDs various sources of degradation, including electrical conditioning and photo-oxidation, are known to result in emission of green light [25, 26]. It is believed that trap sites are formed for electrons, holes or both, leading to emission of lower energy light. These traps are probably formed by chemical reactions with oxygen, leading to ketones.

Applying a high current density (electrical conditioning) will reduce the conductance and luminous efficiency of a device, but can also lead to a significant increase in organic magnetoresistance [27]. Again the exact mechanism is unknown, but the effect can be partially reversed by thermal annealing close to the glass temperature of the polymer. Chemical changes such as oxidation are therefore excluded. The reversibility suggests that conditioning causes morphological changes. These presumably act as trap sites that contribute to the OMAR effect [28].

Rybicki et al. discovered that exposure of an organic device to X-rays can also lead to reduced performance and increased OMAR [29]. Traps were found with a depth of approximately 0.5 eV. Again, these traps are the presumable cause of the high magnetic field effects. These results strongly suggest that OMAR can be enhanced by artificially adding traps to the material.
Chapter 3

Experimental Setup

The first section of this chapter describes the device layout, polymer compositions and fabrication techniques. The second section describes the electrical and optical measurement techniques that have been used.

3.1 Devices and Materials

The organic devices that were used consist of an organic semiconducting layer sandwiched between two electrodes, as shown in fig 3.1. The device is built on a glass substrate covered with a patterned indium tin oxide (ITO) layer, which acts as a transparent hole injection electrode. On this substrate a 50 nm thick layer of poly(3,4-ethylenedioxythiophene) with a poly(styrenesulfonate) dopant (PEDOT:PSS) is spin-coated to smooth the ITO layer and improve hole injection. Next the active organic layer is spin-coated with a thickness of approximately 150 nm. The top electrode consists of a layer of barium followed by aluminium, and is applied by thermal evaporation. The PEDOT:PSS and barium layers improve hole and electron injection respectively because their work functions match the HOMO and LUMO of the organic layer. A more detailed description of the fabrication process is provided in Appendix A.

![Figure 3.1: Cross-section of the used samples. Stated thickness values are approximate.](image)

As active layer three different polymers are investigated, with an increasing amount of traps. The first polymer (B) is a blue light-emitting backbone with an energy gap of approximately 2.8 eV. As the second polymer the backbone with a green dye is used (BG), and as third the backbone with both green and red dyes (BGR). In this report, these polymers and devices
made with them are referred to as blue, blue-green and white respectively. The dyes are components with the same HOMO level, but with LUMO levels that lie 0.35 eV and 0.75 eV lower respectively. Therefore they are assumed to act as electron traps. Their lower energy gaps lead to emission of the green and red light. The structures of these polymers are shown in Figure 3.2.

![Figure 3.2: Structure of the used polymers. The components p and q are the green and red dyes, respectively. The composition of the blue polymer (B) is m = 50%, n = 40%, o = 10%, p = 0%, q = 0%. For the blue-green copolymer (BG): m = 50%, n = 39.90%, o = 10%, p = 0.1%, q = 0% and for the white-emitting copolymer (BGR): m = 50%, n = 39.88%, o = 10%, p = 0.1%, q = 0.02%. Figure obtained from Nicolai [4]](image)

3.2 Measurement setup

Different setups are used to measure the magnetic field dependent effects in the samples. Quick characterizations are performed on the fixed field setup, in which a variable voltage or current can be applied to the device. Two different permanent magnets are mounted on a rotating disk to apply a magnetic field of 14 mT or 83 mT. In this way, basic magnetoconductance measurements can be performed.

3.2.1 Electrical and optical characterization

More extensive measurements are performed using the variable field setup shown in Figure 3.3a. In this setup, the sample and a photodiode are placed between two magnetic field coils, that can be swept from -500 mT to +500 mT. In this way, conductance and luminescence can be measured as a function of the applied voltage (or current) and magnetic field. This and the previously described setup are placed in a nitrogen-filled glovebox to prevent sample degradation by oxygen and moisture.

As mentioned before, an organic device slowly degrades during operation. This results in drift, i.e. the current and luminescence gradually change over time. To separate magnetic field effects from drift the following procedure is used: Prior to a sweep the desired voltage is applied for a period long enough that short time-scale effects are no longer significant. Next forward and backward magnetic field sweeps are performed. A decreasing exponential function is fitted through currents at equal magnetic field, to determine the current drift. This drift is subtracted from the obtained data, and both sweeps are averaged to obtain the MC(B) curve. A more detailed description of the measurement and drift correction methods is given in [17].

Luminescence is measured simultaneously with current, and the same drift correction procedure is used. Since measurements are taken at constant voltage, applying a magnetic field
leads to a change in current and thus automatically a change in luminescence. However, the variable of interest is the intrinsic MEL, i.e. the MEL at constant current. It is assumed that luminescence and current are related as $\text{EL} \sim I^\beta$. Therefore the following correction is used:

$$\text{MEL}_{\text{int}}(B) = 1 + \frac{\text{MEL}_V(B)}{(1 + \text{MC}(B))^\beta} - 1,$$

where $\text{MEL}_V(B)$ is the MEL measured at constant voltage. From now on, only $\text{MEL}_{\text{int}}(B)$ is referred to as the magneto-electroluminescence.

A measurement series typically consists of measurements of the MC and MEL while the voltage is incrementally raised from low to high. Due to electrical conditioning the device morphology and properties will change during operation, especially at higher voltages. Because this is unwanted, the device is first pre-conditioned at the maximum measurement voltage until its properties do not change significantly anymore. Typically this is at 5 V for 1800 s. This ensures that the device properties are constant during measurements.

### 3.2.2 Electroluminescent spectrum

Measuring the electroluminescent spectrum of a device can provide more knowledge about its energetic system, and makes it possible to measure the contribution of trap sites to luminescence effects. The setup shown in Figure 3.3b was built to measure the spectrum of a device and its magnetic field dependence. The spectrometer system consists of a spectrograph (Newport MS260i), back-illuminated CCD (Andor DV420-BV), and collimating and focusing lenses. The sample is placed in an airtight container and connected to a source-meter. Two coils are placed around the sample to apply a magnetic field of up to 10 mT. The entire setup is shielded from ambient light. When measuring at very low light intensities the remaining background light becomes significant, however, and needs to be compensated for.

To measure the magnetic field dependence of the spectrum, a constant current is applied to the sample, and a magnetic field of 10 mT is switched on and off. As with the MC(B) and MEL(B) measurements, compensation for drift is necessary. First, the desired current is applied for a time long enough to remove short time-scale effects. Then five spectra are taken,
with the magnetic field switched on during the second and fourth measurements. Next, a measurement of the background light is made.

The wavelength dependent MEL is then computed as follows:

\[ \text{MEL}_{10mT}(\lambda) = \frac{\frac{1}{2}I_2(\lambda) + \frac{1}{2}I_4(\lambda) - \frac{1}{8}I_1(\lambda) - \frac{3}{4}I_3(\lambda) - \frac{1}{8}I_5(\lambda)}{\frac{1}{7}(I_1(\lambda) + I_3(\lambda) + I_5(\lambda)) - I_{\text{back}}(\lambda)}, \]  

(3.2)

where \( I_i(\lambda) \) is the spectral irradiance of the \( i^{\text{th}} \) measurement, and \( I_{\text{back}}(\lambda) \) the spectrum of the remaining background light. In this way, the drift components up to third order are compensated for.
Chapter 4

Results and discussion

The goal of this project is to investigate if different kinds of traps can be used to manipulate the magnetic characteristics of organic devices. This chapter presents the results of the different measurements and a discussion. First, the general current and luminescence characteristics of the devices are characterized. Next the influence of a magnetic field on conductance, luminescence and the luminescent spectrum is investigated for the three different polymers. Finally the effects of electrical conditioning are investigated.

4.1 Current and luminescence characteristics

In Figure 4.1 the current and luminescence characteristics of a blue device are shown. These measurements were made using the variable field setup without applying a magnetic field. In Figure 4.1a the current density is plotted versus the applied voltage. Three different operation regimes can be observed. Below 2V $J$ increases linearly with $V$. This current is attributed to leakage and is not relevant to magnetic field effects. In the second regime, slightly below the built-in voltage, the exponential Shockley relation is expected. This relation is not clearly visible due to overlap with the other regimes.
In the third regime the current can be attributed to SCLC. A fit using the power law $J = A(V - V_{bi})^\alpha$ gives $V_{bi} = 2.50 \pm 0.01$V and $\alpha = 2.88 \pm 0.02$. The power $\alpha$ is greater than the theoretical value of two in the Mott-Gurney relation, Eq. 2.4. The larger than quadratic voltage dependence might be attributed to the presence of traps according to equation 2.5, meaning that the backbone itself is not trap-free.

Figure 4.1b shows the electroluminescence as a function of the applied current. The curve is fitted with a power law $EL = AI^\beta$ with $\beta = 0.96 \pm 0.01$. This relation is necessary to correct the measured MEL for changes in current according to Eq. 3.1.

4.2 Magnetic field effects

Figure 4.2 shows an example of a measurement made with the variable field setup, according to the procedure described earlier. In this case the MC and MEL of a blue device have been measured as a function of the magnetic field at two different operating voltages, 3V and 5V. The curves follow the typical shape of Figure 2.4b, where both a positive LFE and a positive HFE are visible. The positive low- and high-field magnetoconductance are both predicted by the trion model. The positive low-field MEL can be explained by the fact that more singlet e-h pairs are present due to suppression of spin mixing at the hyperfine scale. Thus more singlet excitons are created, that recombine by emitting light.

Quantitative analysis

In the magnetoconductance curves of Figure 4.2a contributions of different magnetic field scales are present. It is therefore not possible to fit the data using only the non-Lorenzian fitting function (2.11). A double non-Lorenzian curve (2.12) does fit the curve correctly. In this case however, signs of overfitting seem to occur and unrealistic values are obtained for the fitting parameters. To prevent fitting problems, and because the focus in this report lies on the low field effects, only the LFEs are investigated. This is done by fitting a single non-Lorenzian curve through the data between $-50\text{mT}$ and $50\text{mT}$ (dashed lines). This fit provides two parameters, $B_{LFE}$ and $MC_{LFE}$, that provide the field scale and magnitude of
The MEL\((B)\) curves shown in Figure 4.2b show shapes similar to the MC\((B)\). The low-field effects can be fitted in the same way. Especially at low voltages an additional high-field effect can be observed.

4.3 Voltage dependence of MFEs

Measuring the voltage dependence of the magnetic field effects can provide insights on the device physics and the different particle interactions that contribute to the MFEs. Therefore MC\((B)\) and MEL\((B)\) measurements are performed with bias voltages ranging from 2.4V to 5.0V. Each curve is then fitted according to the procedure described above. The MC\(_{\text{LFE}}\) is taken as a measure for the (low-field) magnetoconductance. This is done for the blue backbone polymer, and the two polymers with added traps. In the same way, the effect of traps on the MEL is investigated.

![Figure 4.3: Magnitude of the low-field magnetoconductance as a function of the applied bias voltage, for the blue, blue-green, and blue-green-red polymers. Fits are performed using the trion model.](image)

Figure 4.3 shows the low-field magnetoconductance as a function of the applied bias voltage, for the three different polymers. In case of the blue and blue-green polymers, each data point is an average over multiple samples and the error bar the standard deviation in the average. In case of the white polymer, only the data from one device is shown. The MC in other white devices is of the same magnitude but has too much noise.

The data has been fitted using the analytical expression (2.13) obtained from the trion model with the assumption that \(p = a(V - V_{bi})\). For all three polymers the voltage dependence predicted by the trion model is observed. At voltages just above \(V_{bi}\) a steep increase in MC is measured due to the formation of trions and at higher voltages a decrease, that is attributed to trap filling.

The model predicts an increase in MC when the trap density is increased, but this is not
observed. The addition of green dyes does not lead to a difference in MC at all. A possible explanation for this result is that no trions are formed at the green dyes. Nicolai et al. [4] showed that trap-assisted recombination was not observed at these sites. Both results might be explained by the fact that the green dyes do not act as traps, or that different processes occur than at other types of traps that do not allow trions to form and live long enough.

The addition of the red dyes leads to a sharp decrease in MC, while the shape of the voltage dependence stays the same. This decrease cannot be explained by the trion mechanism, that predicts the opposite. However, this model makes the assumption that all traps are filled. This assumption is likely not correct in this situation. One can estimate the hole density using Eq. 2.14 and the values of $a$ and $V_{bi}$ obtained from the fit. At 2.9 V, where the MC is maximal, this results in $p = 1.2 \times 10^{-5} \text{nm}^{-3}$. Nicolai et al. found a red trap density of $3 \times 10^{-4} \text{nm}^{-3}$. In OLEDs the electron density is assumed to be of the same order as the hole density, leading to an electron density that is an order of magnitude smaller than the trap density.

This means that only a small fraction of the traps is actually filled and can form trions, leading to a lower MC than expected. Furthermore it is likely that the available electrons are captured close to the injection electrode due to the large amount of traps. In the rest of the device only holes contribute to conduction, leading to a lower total current. Therefore the magnetic field effects become smaller relative to the total resistance.

In conclusion, a model that only considers microscopic interactions, such as the trion model cannot explain all of the observed effects. Traps severely affect the physical properties of the device, such as charge density and mobility. A more complete model is needed that also incorporates these macroscopic physical effects.

In Figure 4.4, the magnitude of the low-field MEL is shown as a function of voltage, for the three different polymers. All polymers show a positive effect that decreases with increasing voltage. The positive effect can be explained by electron-hole interactions, but no model ex-

\[ \text{Figure 4.4: Magnitude of the low-field magneto-electroluminescence as a function of the applied bias voltage, for the blue, blue-green, and blue-green-red polymers.} \]
ists that explains its voltage dependence. At high voltages, the MEL converges to a constant value higher than zero. Therefore it can be seen as the sum of a voltage dependent and independent effect.

The addition of the green dye leads to a slight increase in MEL in the regime between 2.8V and 4.0V. Adding the red dye leads to a sharp decrease of the effect, over the entire voltage range. In addition, the MEL becomes less dependent of voltage, changing from 1.4% at 2.8V to 1.0% at 5.0V. In the following section, it is shown that luminescence in the white polymer can mainly be attributed to recombination at the red dyes, which is a trap-assisted process. In the other polymers, Langevin recombination is the dominant mechanism. The sharp decrease in luminescence by adding red dyes suggests that magnetic field effects are less relevant in SRH recombination. However, it is likely that again physics at the device level play a significant role in the MEL.

4.4 Magnetic field dependent spectra

Measuring the luminescence spectrum of a device provides insight about the energetic transitions that occur. To investigate how a magnetic field influences these processes, the spectra of the different polymers are measured with and without applying a magnetic field. Also, the voltage dependence is investigated. To only measure the intrinsic MEL, measurements are taken at constant current. When a voltage is mentioned, it refers to the voltage corresponding to the applied current at zero magnetic field.

![Figure 4.5: (a) Emission spectrum of the blue polymer, normalized to the 433nm peak. (b) Change in the spectrum at 10 mT.](image)

Figure 4.5a shows the spectrum of a blue device measured at different voltages. Instead of a sharp peak, a broad range of wavelengths is present in the emission, which can be related to the energetic disorder in the device. At 5V the distribution is peaked at 433nm, which corresponds to 2.86 eV. As a measure of the spread, the standard deviation can be used, which is 0.12 eV. At lower voltages, the intensity at long wavelengths becomes relatively larger. This suggests that a part of the recombination at these wavelengths is of the SRH type, and thus trap-assisted. This means that states in the lower part of the energy distribution can act as
trap sites, and supports the hypothesis that the blue polymer already contains traps.

In Figure 4.5b the change in the spectrum is shown, when applying a magnetic field of 10 mT. Between 400 nm and 550 nm, the range corresponding to the emission peak, the MEL is positive and largely constant. Between 625 nm and 800 nm a negative effect is observed. The magnitude of the MEL decreases with voltage, which agrees with the earlier results shown in Figure 4.4, but the shape is mostly voltage-independent.

The negative effect takes place in the wavelength range where recombination is thought to be trap-assisted. An explanation might be that at these trap sites the amount of singlets decreases when applying a magnetic field, leading to less light emission. This could be caused by a lower exciton formation rate for singlets than for triplets ($k_S > k_T$), which is the opposite of the conventional assumption. Another explanation is that simply less electrons-hole pairs are formed on trap sites, and more on the backbone when applying a magnetic field. This could be caused by macroscopic mechanisms.

Figure 4.6: (a) Emission spectrum of the blue polymer with green dyes, normalized to the 433 nm peak. (b) Change in the spectrum at 10 mT.

In Figure 4.6a the emission spectrum of a blue-green device is shown for different voltages. The emission at the blue backbone is visible, as well as two contributions from the green dye, peaked at 520 nm and 555 nm, or 2.38 eV and 2.23 eV. The shape of the spectrum only depends on the voltage to a small extent. The relative amount of green emission first decreases and then increases with increasing voltage. Green emission can therefore not be attributed to SRH recombination, which would result in a large decrease with voltage.

Figure 4.6b shows the change in the spectrum at 10 mT. As in Figure 4.4 the change decreases with increasing voltage. Between 400 nm and 600 nm the MEL is mostly constant, but at lower wavelengths it decreases. The decrease becomes sharper at lower voltages. Because the MEL is the same for blue and green emission, it is likely that the recombination process at the blue polymer is magnetic field dependent, and the energy transfer to the green dye is not.

In Figure 4.7a the spectrum of a white device is shown. The addition of the red dye leads to a peak at 625 ± 1 nm at 2.8 V that shifts to 620 ± 1 nm at 5 V. The height of the peak relative to the blue peak strongly decreases with increasing voltage. This means that the red
Figure 4.7: (a) Emission spectrum of the blue polymer with green and red dyes, normalized to the 433nm peak. (b) Change in the spectrum at 10 mT.

emission results from SRH recombination, and thus that the red dyes act as trap sites. In Appendix B, the voltage dependence of the different peaks is analysed more thoroughly.

The magnetic field dependence of the spectrum is shown in Figure 4.7b. The observed MEL is lower than in the other polymers, even in the blue and green wavelength ranges. A clear voltage dependence is now only observed in the blue and green range. The magnetic field dependence of (SRH) recombination at red dyes does not change with increasing voltage.

The lower MEL in the blue and green peaks might suggest that the presence of the red dyes influences the recombination processes in the backbone. However, due to the low concentration of this dye (0.02%), most of the backbone monomers are not in contact with the dye. It seems therefore unlikely that the dyes can directly influence the microscopic processes on the backbone. It is more likely that macroscopic processes that influence the amount of pair forming and recombination play an important role.

The magnetic field effects on an organic semiconductor have been investigated, as well as the addition of two different dyes. The voltage dependence of the MC was consistent with the trion model, but the voltage dependence of the MEL could not be explained. The addition of green dyes did not have any significant influence on the MC, MEL and the magnetic field dependence of the spectrum. The addition of red trap sites does not lead to the expected increase in MC, but to a decrease in both the MC and MEL, and significant changes in the spectral MFEs. The current OMAR models are not able to explain these measurements. In conclusion, a new model is needed that incorporates the physics on both the microscopic and macroscopic level.

4.5 Influence of electrical conditioning

In the previous section the ability of dyes to affect magnetic field effects was investigated. It is also known that electrical conditioning can enhance these effects. This is presumably
caused by the formation of trap sites. However, these traps have not yet been observed in the emission spectrum of a material. Here, the effects of different levels of electrical conditioning on the MC, MEL and spectrum are investigated. As reference a blue device is taken which has been pre-conditioned at 5 V for 1800 s. The device is first conditioned at 6.5 V for 7200 s, and then at 7.5 V for 7200 s. Measurements are taken after each stage.

![Graphs](image)

**Figure 4.8:** Magnitude of the low-field magnetoconductance (a) and magneto-electroluminescence (b) as a function of the applied bias voltage, after different levels of electrical conditioning. The MC is fitted with the relation from the trion model.

In Figures 4.8a and 4.8b the low field effects in the MC and MEL are shown as a function of the applied bias voltage, after different levels of conditioning. In both the MC and MEL a significant increase is observed, which is as expected. These measurements are in accordance with those by Bagnich et al. in SY-PPV devices [28]. In the MC the shape of the voltage dependence is unaltered, but the peak of the effect shifts to higher voltages. The shift can be explained by the fact that a higher charge density is needed in order to fill the increased amount of traps.

### 4.5.1 Spectra

Figure 4.9a shows the spectrum of the blue device after different levels of electrical conditioning. All measurements were taken at a constant current of 0.7 µA. A blue peak is observed at approximately 445 nm, or 2.8 eV, that does not change significantly. An additional peak is observed at 640 nm, or 1.9 eV, that increases in height by conditioning. This peak shows that the increase in MC and MEL is indeed correlated to the formation of radiative trap sites. Recombination at these traps occurs according to the SRH mechanism, as shown in Appendix B.

In Figure 4.9b the magnetic field dependence of this spectrum is shown. Both before and after conditioning the MEL is positive in the blue and green wavelength range, and negative for wavelengths longer than 600 nm, the region where traps are observed. Conditioning leads to an increase only in the blue and green regime, while no significant difference is observed in the magneto-electroluminescence of the traps themselves.
In Figure 4.10 the magnetic field dependence of the spectrum is shown again, but now at different voltages for the situation after conditioning at 7.5 V. The results are similar to the situation before conditioning, but with a higher magnitude of the effect in the blue-green region. In the trap region, above 600 nm, little voltage dependence is observed.

Both the traps created by red dyes and those by conditioning result in changes in the magnetic field effects. The addition of red dyes results in a sharp decrease of the MC and MEL while increasing the amount of intrinsic traps by conditioning has the opposite result. Also, changes occur in the magnetic field dependence of the spectrum. Traps cause the magnetic field dependence of the blue and green emission (< 600 nm) to change significantly. This is remarkable because the traps themselves emit red light (> 600 nm). The changes in the blue-green region are strongly voltage dependent, whereas the changes in the red region are not. None of the existing (microscopic) models, including the trion model is able to explain these results. Again, the conclusion is that a model is needed that includes both microscopic and macroscopic effects.
Chapter 5

Device Model

The experimental results cannot be explained by existing models and suggest that a new, macroscopic model is needed to understand the observations. Here, a model is proposed that is based on trap filling by triplet excitons. This model can qualitatively explain all of the observed magnetic field effects, their voltage dependence, and the difference between the two types of traps. Device simulations incorporating this model are carried out, that result in the correct voltage dependence of the MC and MEL.

5.1 Theory

In the previous chapter it was observed that an increase of the amount of trap sites, with their emission in the red wavelength range, has a strong effect on the magnetic field dependence in the blue and green wavelength ranges. This suggests that these trap sites have a significant effect on the device processes and their magnetic field dependence.

The new model is based on capturing of triplets on trap sites. This capturing mechanism is similar to that of SRH recombination. First an electron is captured at a trap, after which a hole can diffuse toward the site. The two particles form an e-h pair, that becomes an exciton when the hole and electron are at the same site. Again, singlet and triplet pairs are formed in the statistical 1:3 ratio. Spin mixing occurs between these pairs, resulting in a S-T exciton ratio different than 1:3.

So far there is no difference with the e-h pair mechanism that is illustrated in Figure 2.6. Now, suppose that the exciton formation rate is higher for singlets than for triplets ($k_S > k_T$). This is the opposite situation as with Langevin recombination. Spin mixing will thus lead to a higher amount of singlet excitons. These will quickly recombine and free the trap. Triplets cannot recombine directly will stay trapped for a much longer time. In this new model, these trapped triplets have a significant impact on the processes in the device.

Because triplets are assumed to live very long, they occupy a large fraction of the available trap sites. Due to their neutral charge, excitons do not contribute to space charge effects and do not hinder the current. Meanwhile there are less unoccupied traps left that can capture electrons. This leads to a higher electron mobility and more free electrons, which is illustrated in Figure 5.1.
Now, if a magnetic field is applied, spin mixing is suppressed. This leads to a higher amount of trapped triplets, and less unoccupied traps. Because more traps are already occupied by triplets, less electrons can be captured. More free electrons are thus present in the device and their mobility is higher. This leads to a higher current, and more electrons that can recombine on the backbone polymer. Meanwhile less singlets are formed at trap sites, leading to a less light emission from the (red) traps.

If we apply the model to the blue polymer, where intrinsic traps are present, it can explain the observed magnetic field effects. The positive MC and increase in Langevin recombination on the host polymer are caused by a higher amount of free electrons when a magnetic field is applied. The decrease in recombination on the traps is due to the lower amount of singlets that are formed there.

The voltage dependence of the MC and MEL can also be explained. The sharp, linear increase in MC at low voltages results from the linear increase in exciton formation, given by the SRH equation (2.7). The decline at higher voltages is due to trap filling. The amount of excitons rises no longer while the density of free polarons still increases. Therefore, the effect of the excitons becomes less important.

As mentioned before, the MEL can be split in a contribution that decreases with voltage, and a constant part. The first can be attributed to the trapped triplet mechanism, and declines with voltage. The constant part follows from the electron-hole pair interactions on the backbone polymer itself. The MEL caused by these interactions is not voltage dependent. For the same reason, the MEL at the traps is independent of voltage. Increasing the amount of trap sites would enhance the MC and MEL for Langevin recombination. This is indeed observed when more traps are created by electrical conditioning.

The model can also be applied to the blue polymer with red dyes added. The difference is that for these traps, the exciton formation rate is assumed lower for singlets, which is also the case on the backbone \((k_S < k_T)\). Spin mixing now results in a higher number of triplet excitons, which reduces when applying a magnetic field. The contribution to the MC and MEL for blue and green emission are now negative, while the MEL at the traps is positive. This exactly agrees to the observed results.
In case of the blue polymer, the MEL is explained by a total increase in Langevin recombination. But this also leads to an increased amount of triplet excitons on the backbone. The simultaneous increase in both singlets and triplets under a magnetic field has been reported before by Nguyen et al. [30] and Reufer et al. [31]. In the latter case, the experimental data was inconsistent with the electron-hole pair and exciton-charge mechanism. Both findings can, however, be explained by the trapped triplet model.

5.2 Device simulations

The new model provides a qualitative explanation for the observed effects. Simulations are performed to make an initial quantitative verification, using an existing numerical drift-diffusion method. Here, a short description of this method is presented. More information is given in Appendix C, and by Cox et al. [3, 32].

The model solves the one-dimensional continuity, drift-diffusion, and Poisson equations for electrons and holes. The effects of traps and triplet excitons are also incorporated into this model. Polaroncs are allowed to recombine through both the Langevin and SRH mechanisms. Upon recombination, triplet and singlet excitons are formed with a certain ratio. To simulate spin mixing, the singlet:triplet ratio is made magnetic field dependent. At high magnetic fields, when spin mixing is suppressed, this is equal to the statistical ratio 1:3. At zero magnetic field, the ratio is either lower or higher, depending on which exciton formation ratio is larger. The MC is then calculated as the relative difference between the two situations. The same is applied to the total amount of Langevin and SRH recombination.

Simulation results are shown in Figure 5.2. The MC was calculated as described above, and for the MEL the relative difference in Langevin recombination is taken, corrected for the increase in current. Simulations have been performed for different values of the applied potential difference. Close to the built-in voltage, a sharp increase of the effect can be seen and at higher voltages, a decrease is observed. The obtained MC curve thus agrees well with the
experiments on blue devices, except that the magnitude of the effect is lower. This probably results from the specific choice of parameters, but this has not been investigated yet. Note that the effect is negative below the built-in voltage. During the experiments, no data was taken in this region.

The MEL curve also shows an increasing, and then decreasing trend, but its peak is shifted to lower voltages. The decrease at higher voltages agrees very well with the experiments, but the increase at low voltages does not. No experimental data exists of the luminescence near the built-in voltage, because the light intensity was too low to be measured accurately. Furthermore it is not yet exactly known how the shape of the curve depends on the simulation parameters.

For this model to work, two assumptions are needed. For the intrinsic traps, the exciton formation rate needs to be higher for singlets than for triplets. This is the opposite of what is generally assumed in OMAR models. However, there is no fundamental reason that requires one of these rates to be higher. Higher singlet formation rates have been assumed before [33]. Another assumption is that the lifetime of trapped triplets is sufficiently long to be able to influence the polarons in the device. During simulations, a lifetime in the order of milliseconds was required. In the literature, lifetimes are usually in the order of tens of microseconds. Baldo and Forrest [34] obtained a value of $25 \mu s$ in Alq$_3$ devices. However, this considers free triplets, that are thought to diffuse throughout the device and quench at interfaces and defects. Trapped triplets are immobile and can not be quenched in this way, which would explain the longer lifetimes.

The newly developed model not only explains the results found in the experiments and earlier literature, but also predicts the voltage dependence of the MC and MEL, that is seen in many devices. The mechanism is relatively simple, and is based on reasonable assumptions. Still, the model explains most experimental results only qualitatively. Further simulations need to be performed to gain quantitative insight in the influence of different parameters. Developing an analytical expression based on the model is also a possible improvement.
Chapter 6

Conclusions

In this chapter, the main conclusions of this work are summarized. Finally an outlook is given on future research possibilities.

6.1 Creating traps by copolymerization

During this project, the influence of trap sites on magnetic field effects in organic semiconductors was investigated. A blue backbone polymer was used in which different kinds of traps were created. In the backbone polymer itself the following effects were observed:

- A positive magnetoconductance of up to approximately 5\% was measured. The effect showed a steep increase for voltages just above the built-in voltage, and decreased again at higher voltages.

- A positive magneto-electroluminescence was observed as well, with a maximum of approximately 11\%. The effect decreased with increasing voltage.

- The EL spectrum of the device was peaked in the blue wavelength range, at around 433 nm, and extended towards approximately 800 nm. The small amount of red light emission is believed to be caused by intrinsic traps.

- When a magnetic field was applied, an increase in intensity was observed for wavelengths shorter than 600 nm, and a decrease for longer wavelengths. The effects for short wavelengths strongly decrease with increasing voltage.

The positive MC and MEL are consistent with earlier experimental results reported in the literature. However, the measured change in the EL spectrum when applying a magnetic field has not been observed before.

The first method of artificially creating trap sites was the incorporation of a monomer (dye) with a narrower band-gap into the host polymer. Two different dyes were used, emitting green and red light respectively. The addition of the green dye did not have a significant influence on any of the observed magnetic field effects.

Further addition of a red dye did have a large effect on these effects. The following changes were observed:
The MC was decreased in magnitude by approximately 4.3 times, while the voltage dependence remained the same.

In the MEL a decrease was observed of up to 6 times. The resulting MEL was largely constant with increasing voltage.

Several differences were observed in the magnetic field dependence of the spectrum. For wavelengths shorter than 600 nm, the effect was still positive, but much smaller. For wavelengths longer than 600 nm, the effect turned from negative to positive, and was independent of voltage.

The fact that the red dyes do influence the magnetic field effects whereas the green dyes do not is probably caused by the difference in recombination mechanism. From both the experiments and the literature can be concluded that on the red dyes SRH recombination occurs. This is a trap-assisted process. On the green dyes, the relevant process is Förster Resonance Energy Transfer. This could mean that the green dyes do not act as trap sites.

The decrease in MC and MEL caused by the addition of the red dye could not be explained by any of the existing models, including the electron-hole pair mechanism and exciton-charge mechanisms. The trion model assumes traps as the origin of OMAR and therefore predicts an positive relation between the amount of traps and the magnitude of the MFE’s. The experiments showed the opposite and thus question this model.

The magnetic field dependence of the spectrum showed that traps could influence the recombination processes on the backbone of the polymer. This has not been observed before and could not be explained by any of the contemporary OMAR models. The reason is that these models are only based on local interactions between particles and their spins. They can, therefore, not explain the effects of traps on recombination at different locations in the device. The experimental results strongly suggest that a new model is needed, that is based on both microscopic and macroscopic processes.

### 6.2 Creating traps by electrical conditioning

Emission of red light by the blue polymer without dyes suggests that this polymer already contains trap sites. It was found that the amount of these traps could be increased by electrical conditioning at relatively high voltages. This provides a second way of artificially adding traps to a device. The following effects were observed:

- Increasing amounts of electrical conditioning led to an increasing peak in the emission spectrum at 640 nm. The emission could be attributed to SRH recombination, which suggests the presence of traps.
- The MC was increased by a factor 2.5. The shape of the voltage dependence was unchanged, but the peak had shifted towards a higher voltage.
- A significant increase was observed in the MEL as well, while the decreasing behaviour with voltage stayed the same.
Changes were observed in the magnetic field dependence of the spectrum. For short wavelengths (< 600 nm) the magnetic field effect was increased. For wavelengths longer than 600 nm the effect was still negative, and equal to before conditioning.

The increase in MC and MEL by conditioning was reported in the literature for different polymers. The formation of traps had been proposed before, but no direct evidence was found. The measurements of the emission spectrum, and its voltage dependence performed during this project confirm that electrical conditioning indeed creates trap sites.

The effect of conditioning on the magnetic field dependence of the spectrum has not been observed before. Remarkably, a large increase in MFE’s occurs in the short wavelength region, while the traps themselves emit light of longer wavelengths. As with the red dyes, the presence of these traps has a major influence on the recombination process at the backbone of the polymer.

The observed increase in MC and the voltage shift can perfectly be explained by the trion model, that regards traps as the origin of magnetoconductance. However, none of the current models can explain the changes in MEL, and the magnetic field dependence of the spectrum. The reason is the same as before: contemporary models only consider microscopic processes.

6.3 New device model

The two types of traps that were investigated show striking differences. The dyes resulted in a decrease in MC, MEL, and magnetic field dependence of recombination on the backbone. On the other hand, the magnetic field dependence of emission from the dyes themselves was positive. Exactly the opposite effects were observed when traps were created by electrical conditioning.

A new and relatively simple model was proposed, that explains both the influence of traps on processes on the backbone, and the difference between the two types of traps. Numerical simulations have shown that it also leads to the correct voltage dependence of the MFE’s. The proposed model is novel in that it considers effects at the (macroscopic) device level, instead of only local interactions between particles. The central idea is that traps can capture triplet excitons, which influence the free electron density in the rest of the device. The amount of triplets is magnetic field dependent due to spin mixing, which causes different magnetic field effects.

The strength of the model is that it can explain a variety of observations, including those found in the literature, using a simple mechanism with little assumptions. Still, it provides mostly qualitative explanations. To verify the correctness of the model, it must be shown if it also quantitatively agrees with experiments.

6.4 Outlook

This project showed that traps are indeed important to the origin of MFEs in organic materials. It also showed that mechanisms at the macroscopic level are essential in explaining
these effects. Furthermore, it proves that measuring the magnetic field dependence of a device spectrum can provide valuable information of the trap characteristics. However, it did not only answer questions, but also raised new ones. During this project, different results were attributed to the addition of red dyes. However, these were added to a polymer in which green dyes were also present. A blue polymer with only red dyes was not available to us. Performing the same experiments on such a polymer is needed to exclude possible effects of the green dye.

It was shown that increasing the number of intrinsic traps in the blue light emitting polymer results in higher magnetic field effects. Therefore it might be possible to create a device with certain desired MFEs by manipulating the amount of traps. To develop such a device, one can experiment with different backbone-dye combinations, or different ways of creating additional traps. For example, earlier research suggests that traps can be formed by exposure to oxygen or X-ray radiation.

The new device model still needs to be verified or falsified in a quantitative way. That can be done by performing numerical simulations with different parameters, and comparing the results with experiments. For example, one can experiment with different trap densities by altering the dye concentration. Other parameters can also be manipulated. Furthermore, one can try to develop analytical expressions from the model, or improve it by including more effects. All traps were the same in our model, but it is possible to add different types of traps, such as intrinsic ones and dyes. A better model can provide more knowledge about organic materials, and help in the engineering of OMAR-based devices.
Bibliography


Appendix A

Sample fabrication process

This appendix contains an overview of the fabrication process of the OLED devices. All details specific to the devices used in this project are given. A more extensive description of the procedure is given by Cox [35]. All devices were fabricated using the following process:

Preparing solutions
The polymer in solid form is dissolved in toluene to create a solution of 12 mg/ml. Different concentrations are needed when using other polymers, or when a different thickness is desired. For example, a concentration of 10 mg/ml led to a thickness of 90 nm.

Preparing substrates
Devices are made on top of a glass substrate, which is covered with a patterned ITO layer. Substrates are cleaned prior to spin coating.

Spin coating
First, the PEDOT:PSS layer is spin coated at 3000 rpm for one minute. This layer is then thermally annealed at 100 °C for 20 minutes. Then, the active layer is spin coated at 1200 rpm for 1 min.

Metal evaporation
Next, the substrates are placed in a metal evaporator inside a glovebox. Predefined programs are used to deposit a 5 nm Ba layer, and an Al layer of 100 nm. Finally, the finished devices are transported to the measurement setup.
Appendix B

Voltage dependence of luminescence

According to equations 2.6 and 2.7, the amount of Langevin recombination scales quadratically with the charge carrier densities, while SRH recombination scales linearly. The charge density can be related to voltage according to equation 2.14. By investigating the voltage dependence of a certain peak in the emission spectrum, one can therefore determine the relevant recombination mechanism. Because emission of blue light on the backbone results from Langevin recombination, it scales according to Eq. 2.6. By measuring the height between a certain emission peak relative to the blue peak, one can determine the recombination mechanism. In the case of Langevin recombination, this ratio should be independent of voltage. In the SRH case, the ratio should scale as

\[
\frac{R_{\text{SRH}}}{R_{\text{Langevin}}} \propto (V - V_{\text{bi}})^{-1}.
\]  

(\text{B.1})

![Graph showing the voltage dependence of peak height relative to blue emission.](image)

\textbf{Figure B.1: Ratio of green peak at 520 nm and the red peak of 420 nm to the blue peak of 433 nm, in a white OLED device. The red:blue ratio has been fitted with the power function } A + B/(V - V_{\text{bi}}), \text{ and the green:blue ratio with a constant value.}
Figure B.1 shows the height of the green and red peaks relative to the blue peak, in a white device. Clearly, the ratio green/blue is independent of voltage, showing that green emission must result from Langevin recombination. The relative height of the red peak has been fitted with a power function and indeed scales as Eq. B.1. Red emission thus results from SRH recombination.

Figure B.2: Red graph: Ratio of the red (640 nm) peak to the blue (445 nm) peak in the electrically conditioned blue device. Black graph: Ratio of SRH and Langevin recombination obtained from drift-diffusion simulations. Both are fitted with $A + B/(V - V_{bi})^r$, with $r = 5.2 \pm 0.7$ and $r = 1.74 \pm 0.05$ respectively.

Figure B.2 shows the red:blue ratio, in the blue device that was electrically conditioned at 7.5 V. Also shown is the ratio of SRH (trap-assisted) and Langevin recombination obtained during device simulations. Both show a similar decreasing trend with voltage, which indicates SRH recombination at trap sites. The power $r$, however, is not equal to one in both cases. This can be explained by the fact that Eq. 2.14 is based on a simplified device model, that ignores traps. The presence of traps increases the complexity of the device physics and leads to a non-linear behaviour.
Appendix C

Device simulation details

This appendix provides a short description of the model that is used in the device simulations. Further information about the model, including boundary conditions, can be found in [32]. This model is based on the drift-diffusion equations for electrons and holes along one direction in the organic device.

The numerical device model solves the continuity equations for electrons and holes:

\[
\frac{\partial n}{\partial t} = \frac{1}{q} \frac{\partial J_n}{\partial x} - r_{pre} \gamma n p - \gamma n N_t (1 - f_t), \quad (C.1)
\]

\[
\frac{\partial p}{\partial t} = -\frac{1}{q} \frac{\partial J_p}{\partial x} - r_{pre} \gamma n p - \gamma R n_t p, \quad (C.2)
\]

the rate equations for trapped electrons and triplets:

\[
\frac{\partial n_t}{\partial t} = \gamma_t n N_t (1 - f_t) - \gamma_R n_t p, \quad (C.3)
\]

\[
\frac{\partial T}{\partial t} = P_T(B) \gamma_R n_t p - [\gamma_T P(n + p) + k_T] T, \quad (C.4)
\]

the drift-diffusion equations for electrons and holes:

\[
J_n = q \mu_n n \frac{\partial \Psi}{\partial x} + q D_n \frac{\partial n}{\partial x}, \quad (C.5)
\]

\[
J_p = q \mu_p p \frac{\partial \Psi}{\partial x} - q D_p \frac{\partial p}{\partial x}, \quad (C.6)
\]

and the Poisson equation:

\[
\epsilon_0 \epsilon_r \frac{\partial^2 \Psi}{\partial x^2} = q(n - p). \quad (C.7)
\]

Here \( n \) and \( p \) are the electron and hole densities, and \( J_n \) and \( J_p \) the currents attributed to these particles respectively. \( \Psi \) is the electric potential, \( n_t \) the density of trapped electrons, and \( T \) the trapped triplet density. The occupation of the trap sites is \( f_t = (n_t + T)/N_t \), and the diffusion coefficients for electrons and holes are \( D_n = k_B T/q \mu_n \) and \( D_p = k_B T/q \mu_p \). The
Simulation parameters are given in Table C.1.

Langevin recombination is incorporated into this model by adding the recombination term $-r_{pre} \gamma_{np}$ to the continuity equations for electrons and holes. The effects of traps are included by adding the electron trapping term $-\gamma_t n N_t (1 - f_t)$, and hole trapping by a captured electron $\gamma_R n t p$. Extra information about the effect of traps in this model can be found in [3].

The influence of a magnetic field is included in the parameter $P_T(B)$, the fraction of the excitons that are formed in triplet configuration. At zero magnetic field, spin mixing lowers the amount of triplets and a value of 0.70 is chosen. When spin mixing is suppressed by a magnetic field, the value of this parameter is the statistical value 0.75.