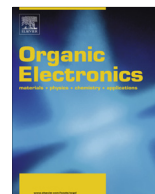




ELSEVIER

Contents lists available at ScienceDirect

## Organic Electronics

journal homepage: [www.elsevier.com/locate/orgel](http://www.elsevier.com/locate/orgel)

# The influence of the triplet exciton and charge transfer state energy alignment on organic magnetoresistance



Paul Janssen, Steinar H.W. Wouters, Matthijs Cox, Bert Koopmans\*

Department of Applied Physics, Center for NanoMaterials (cNM), Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

## ARTICLE INFO

## Article history:

Received 4 July 2013

Received in revised form 10 January 2014

Accepted 12 January 2014

Available online 24 January 2014

## Keywords:

Organic magnetoresistance

Magnetic field effects

Magnetoconductance

Organic semiconductors

Triplet energy

Doping

## ABSTRACT

Recently, it was discovered that the current through an organic semiconductor, sandwiched between two non-magnetic electrodes, can be changed significantly (up to 25%) by applying a small (a few millitesla) magnetic field. At present, the microscopic mechanisms underlying this so-called organic magnetoresistance (OMAR) are intensively being debated. One of the mechanisms which can successfully describe the magnetic field effects on the current in pristine organic semiconductor devices uses the reactions of triplet excitons and polarons. Here, we present a proof of concept study in which we tune these interactions in the device by deliberately doping our devices with fullerene, creating additional charge transfer states (CTS). By engineering devices with different energetic alignments of the CTS and triplet exciton, we can influence the triplet exciton density in the device. We correlate pronounced changes in the magnetic field effect magnitude and lineshape to the energy of the CTS with respect to the triplet exciton.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

The discovery of surprisingly large, room temperature, magnetoresistance effects in organic semiconductor devices without any ferromagnetic components has puzzled the young field of organic spintronics during the past decade [1–3]. The effect is often referred to as organic magnetoresistance (OMAR). The possibility to obtain large (up to 25%) changes in the current at room temperature, while applying only small (a few millitesla) magnetic fields, makes this effect interesting for future applications and, moreover, from a scientific point of view. Studying OMAR provides a deeper fundamental understanding of spin-physics and charge transport in organic semiconductor devices.

All contemporary models explaining OMAR rely on magnetic field dependent reactions of the spin carrying particles, where a magnetic field suppresses the spin mixing of the particle pairs prior to the reaction. There is, however, an active debate about the nature of the particles

(e.g. electrons, holes, bipolarons, excitons or trions) and the exact underlying mechanism influencing the current [4–13]. Currently, the possible mechanisms can be divided into two main categories: (i) mechanisms which only need one type of charge carrier or (ii) mechanisms which need both charge carriers. In the first class, the so-called bipolaron mechanism [6] has been successfully applied to explain magnetic field effects in unipolar devices [8,14,15]. In the second class, we can distinguish between models which describe the reactions of polarons with opposite charge into excitons [4] and models which rely on the spin dependent reactions of triplet excitons with polarons [5,12]. Besides the microscopic models, it is also important to be aware of the highly non-trivial role played by the device physics in order to explain experimentally observed magnetic field effects (MFEs) on the current [16,17]. Very recently, we have shown that the dominant mechanism for OMAR depends on the exact material choice and operating conditions of the device [15] and that the MFE in pristine organic semiconductor devices are predominantly governed by the reactions of (trapped) triplet excitons and polarons [12].

\* Corresponding author.

E-mail address: [b.koopmans@tue.nl](mailto:b.koopmans@tue.nl) (B. Koopmans).

To study the underlying mechanism of triplet–polaron interactions, an exquisite control over the triplet exciton density is desired. In line with earlier work [8,15], we propose polymer–fullerene blends as an ideal model system. We study the influence of triplet excitons on OMAR by introducing a low concentration of fullerene in the polymer devices. This creates additional charge transfer states (CTS) by which the number of triplet excitons can be increased, stabilized or decreased, depending on the relative energetic alignment of the CTS with respect to the triplet exciton [18]. Different energetic alignments can be engineered by choosing the right material combinations [19].

## 2. Theory

### 2.1. Magnetic field effects

As introduced in the foregoing, mixing of spin states plays a crucial role in OMAR. In this section we will show how spin mixing can lead to magnetic field effects on the current. We start our discussion with MFEs in pristine polymer devices. Fig. 1 presents an energy diagram of the relevant spin dependent transitions from free charges to the ground state. Free charges can form precursor pairs in a singlet  $^1(e+h)$  or triplet  $^3(e+h)$  configuration. Within the precursor pairs the separation between the two carriers is such that exchange interactions are still negligible. This enables hyperfine fields, originating from the hydrogen nuclei in the organic material, to mix the singlet and triplet precursor pairs. An external magnetic field suppresses this mixing. From the precursor pair state, the electron–hole pair can recombine into a singlet (S) or triplet (T) exciton and thereafter to the ground state.

In the absence of a magnetic field (Fig. 1b), spin mixing increases the number of triplet excitons if the formation rate of triplets is larger than that of singlets [11]. This is indicated by process  $ISC_{eh}$  in Fig. 1b. Triplet excitons can decrease the current by interacting with free charge carriers [5,12]. Increasing the magnetic field (Fig. 1a) reduces the triplet formation and thus reduces the triplet–polaron interactions and thereby increases the total current, leading to a positive MC. This magnetic field effect, which is governed by the hyperfine field strength experienced by the precursor pair, will be referred to as a low field effect (LFE) and has a linewidth of a few millitesla.

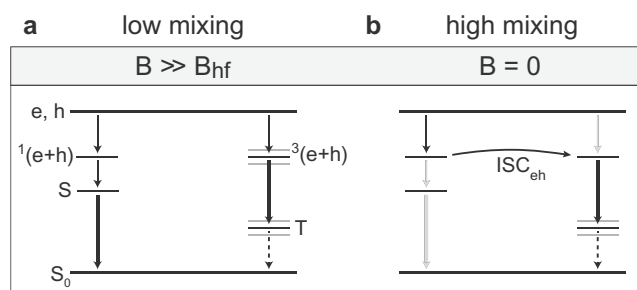
The LFE in the pristine polymer device can be accompanied by a distinct magnetic field effect at ultra-small field scales (USFE, typically  $\leq$  mT) as has recently been demonstrated [11,20]. Moreover, the triplet–polaron interaction is also magnetic field dependent, leading to so-called high field effects (HFE) occurring at field scales on the order of the zero-field splitting (ZFS, typically 100 mT) of the triplet exciton. When describing the triplet–polaron interactions using a mechanism where (trapped) triplet excitons temporarily capture free polarons into meta-stable trions, as proposed by Cox et al. then this HFE results in a positive MC.

### 2.2. Introducing additional states

To further investigate the underlying mechanism of triplet–polaron interactions, we are going to control the triplet exciton density by introducing additional states in the energy diagram. Hereby, the number of triplet excitons can be increased, stabilized or decreased. As introduced, this can be accomplished by adding fullerene to the polymer devices. At low concentration, the fullerene effectively quenches singlet excitons into weakly bound, spatially separated charge transfer states (CTS), where the hole resides on the polymer and the electron on the fullerene. The effect of fullerene on the triplet excitons depends on the energetic alignment of the CTS and triplet exciton, where three different kinds of devices can be distinguished.

First, in device type I, where the triplet exciton lies higher in energy than the CTS, the triplet exciton will also be effectively transferred into a CTS in a triplet configuration, as depicted by process  $T \rightarrow CTS$  in the top panel of Fig. 2. When both states are energetically aligned, the CTS and triplet exciton are in equilibrium and an increase in the number of triplet excitons will be stabilized by the CTS, as indicated by process  $T \leftrightarrow CTS$  in the middle panel of Fig. 2. Finally, in device type II, the triplet exciton lies lower in energy than the CTS and the number of triplet excitons can increase by a back-transfer from the triplet CTS, as shown by process  $CTS \rightarrow T$  in bottom panel of Fig. 2.

The introduction of a CTS can have profound effects on the MFEs, since the number of triplet excitons, ultimately responsible for the magnetic field effect on the current, can be changed significantly in this manner. We will now briefly explain the MFEs. In device type I, CTS decrease the



**Fig. 1.** Energy diagram of relevant spin dependent transitions (indicated by the arrows) from free charges to the ground state in a pristine device. (a) In a large external applied magnetic field, free charges can form precursor pairs in a singlet  $^1(e+h)$  or triplet  $^3(e+h)$  configuration. From this pair state, the precursor pair can recombine into a singlet (S) or triplet (T) exciton. (b) Without a magnetic field, singlet and triplet precursor pairs can mix due to hyperfine interactions, as indicated by transition  $ISC_{eh}$ .

Download English Version:

<https://daneshyari.com/en/article/10566067>

Download Persian Version:

<https://daneshyari.com/article/10566067>

[Daneshyari.com](https://daneshyari.com)