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Pulsed magnetic resonance

of Alq_3 OLED detected by electroluminescence

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Abstract

The aim of the present work is to investigate the nature of spin dependent processes in an organic light emitting diode based on a ITO/ α-NPD/Alq3 structure. The electroluminescence time response of the sample is monitored while the OLED is exposed to a high power resonant microwave pulse. Measurements are carried out at room temperature. The time scale of the induced transition is found to be independent of the bias voltage. It is shown, by way of a simulation, that this behavior **appears inconsistent with** models which attribute a change in the electroluminescence to a variation in charge mobility. Spin dependent processes directly related to a change in the rate of charge recombination play therefore a relevant role in Alq_3 light emitting diodes.

Keywords

Organic semiconductors; Magnetic field effects; Spin dependent processes; OLED; Optically detected magnetic resonance

1. Introduction

The discovery of a large intrinsic magneto-resistance in organic thin films and light emitting diodes triggered a novel interest in spin processes in carbon based semiconductors although this topic was already debated at length in the past [1-5]. Nowadays, the study of organic magneto-resistance (OMAR) is of great importance in the framework of organic spintronics and it introduces a new scenario of possible applications [6, 7]. Spin dependent charge recombination, spin blocking bipolaron formation and triplet-polaron scattering were proposed as possible explanations [8-10]. Furthermore, experimental evidence showed that trapping centers may be related to OMAR, suggesting that more mechanisms may participate to the magneto-resistance [11]. For this reason, recent publications turned the focus of attention to the time response of this phenomenon. Investigations on the magnetic field frequency dependence led to hypothesize that OMAR may be due to a change in minority charge mobility [7, 12]. This possibility was further confirmed by time of flight measurements performed on Alq_3 thin films, which showed that carrier mobility can be affected by the magnetic field [13]. Continuous wave (CW) magnetic resonance techniques were also used as alternative methods to investigate spin effects in organic semiconductors [4, 5, 14-16]. However there are very few papers on time resolved studies, in spite of the abundance of information that these techniques can provide [17, 18]. Moreover most work was performed at low temperature, but it was shown that different phenomena come into play at room temperature where the magnetic resonance signal and organic magneto-resistance change sign [14, 19]. In view of this, pulsed electroluminescence detected magnetic resonance (p-ELDMR) is employed to investigate the time response of spin dependent processes in Alq_3 based organic light emitting diodes (OLEDs) at room temperature.

2. Experimental

The device studied in this work is a multilayer OLED based on small molecules organic semiconductors. The structure consists of a positive electrode (indium tin oxide) deposited on quartz, a hole injector layer of copper phthalocyanine (CuPc 12 nm), a hole transport layer of N,N_-diphenyl-N,N_-bis(1-naphthyl)-1,1_-biphenyl-4,4_-diamine (α-NPD 40 nm), a 60 nm layer of Tris(8-hydroxyquinolinato)aluminum (Alq_3) used as both electron transport and recombination layer, a 0.8 nm LiF layer for electron injection and an electrode of aluminum. The device active area dimensions are 3 mm x 2 mm. More details on sample preparation are provided elsewhere [20]. To avoid air and water contamination, the sample is sealed inside an EPR quartz tube before being exposed to air. Electron magnetic resonance is obtained using a cylindrical X band sapphire resonator placed inside a magnet. The loaded cavity shows a resonance at 9.139 GHz with a Q factor of 300. The microwave (**MW**) power, generated by a continuous wave source, is amplified up to 30 W by a solid state pulsed amplifier. Before amplification, a cascade of two switches is used to create the pulse pattern. Light coming out of the resonator is focused into a light guide and directed to a fast photomultiplier for detection. Further amplification provided by a 50 MHz trans-impedance amplifier sets the minimum rise time detectable by the system (17 ns). A control measurement with a faster amplifier (400 MHz) is performed to rule out any filtering effects.

3. Results

In a typical pulsed ELDMR experiment the sample is irradiated with a high power MW pulse with the magnetic field set to meet the resonance condition. Induced variations in the light electroluminescence are then probed. To increase the stability and lifetime of the device, the bias voltage is applied just for the time needed to stabilize the photo-emission and perform the measurement. This procedure is cycled to average the final signal several hundred thousands of times. An important difference with standard pulsed EPR is that the signal can be probed both during and after the pulse since the optical detector is completely decoupled from the MW circuit. A relevant positive variation of light emission is observed at any field, possibly because of MW induced currents or temperature variations. However the response is very different when the applied field meets the resonance condition for spin 1/2 carriers (see inset in *Fig. 1*). To remove the background, a signal acquired at 320 mT is subtracted from all the data following a similar procedure as reported in [17]. In *Fig. 1* the response of the sample electroluminescence to a 1 μs pulse is shown for different bias voltages. **An electroluminescence quenching of 0.2 % at 6 V occurs during the MW pulse followed by a recovery to the stationary condition. The amplitude of the quenching is found to decrease with increasing voltage. In the figure,** data are normalized **to make clear** the temporal evolution. **The rise time is found to decrease with increasing MW power while the recovery time (~ 200 ns decay half-life time) is found to be unchanged.** No strong effect on both the rise and decay times emerges from varying the bias even though low voltage transitions look slightly faster. The transitions observed under magnetic resonance occur in a sub micro-second time scale. This time scale is significantly smaller than the typical electronic time response of the device **which is also bias dependent as suggested by impedance spectroscopy measurements (not reported here)**. **Changes in the mobility lead to a different space charge stationary distribution that in turn results in a different light emission rate. The time of such a rearrangement of space charge is expected to be bias dependent like the electronic time response. This would be in contradiction from the data reported in *Fig. 1*. To confirm this hypothesis, a space charge limited model is used in the following section.**

4. Simulations and discussion

Bipolar transport and light emission in OLEDs can be described using space charge limited current models [21, 22]. These models have proved to be very reliable in simulating transient electroluminescence experiments [22]. In this paper a similar approach is used to highlight how the light emission deviates if the mobility of one of the two carriers suddenly changes. A simplified model, consisting of a single 100 nm thick Alq_3 layer with ohmic electrodes, is considered since a quantitative comparison is beyond the scope of this work. The equations used to simulate the system are [21]:

(1) $J_e(x,t) = e\mu_e(x,t)n(x,t)E(x,t);$ (2) $\frac{\partial n(x,t)}{\partial x} = -\frac{1}{e}\frac{\partial J_e(x,t)}{\partial x} - r(x,t)p(x,t)n(x,t);$

(3) $J_h(x,t) = e\mu_h(x,t)p(x,t)E(x,t);$ (4) $\frac{\partial p(x,t)}{\partial x} = \frac{1}{e}\frac{\partial J_h(x,t)}{\partial x} - r(x,t)p(x,t)n(x,t);$

(5) $r(x,t) = \frac{e}{\varepsilon\varepsilon_0}[\mu_e(x,t) + \mu_h(x,t)];$ (6) $\mu_e(x,t) = \mu_{e,0}\exp\left(\sqrt{E(x,t)/E_0}\right); \quad \mu_h(x,t) = \mu_e(x,t)/10;$

(7) $\frac{\partial E(x,t)}{\partial x} = \frac{e}{\varepsilon\varepsilon_0}[n(x,t) - p(x,t)];$ (8) $\int_0^d E(x,t)dx = V - V_{built-in};$

Where *d* is the thickness of the layer, $V_{built-in}$ is the built in voltage due to the mismatch between the two electrodes work functions and $\mu_{e,0}$ and E_0 are *1.2 x* 10^{-9} m^2/Vs and *1.952 x* 10^8 *V/m*, respectively [21]. The one dimensional simultaneous equations are solved using a finite difference method. The Alq_3 layer is divided in 200 cells each having given hole and electron densities. The electrical field is defined for both cells and cell interfaces. The electrical field at the interfaces is calculated by using Eq. 7 and 8 whereas the electrical field within the cells by averaging the electrical field at the surrounding interfaces. A uniform electrical field and no space charges are set as starting conditions along the layer. To simulate the ohmic contacts, a proportionality relationship is used between the injected current and the electrical field at the contact. It can be easily seen that if the constant of proportionality is big enough the space charge limited current regime is set and the simulation result is independent of the value of the constant [21]. **The reliability of the model is confirmed by comparing the steady state solutions from the simulations with the Parmentier and Ruppel theory [23]. For this check, mobilities are chosen to be independent from the electrical field, and the recombination coefficient $r(x,t)$ is set to be one thousand times smaller than the Langevin recombination in order to meet the validity conditions of the theory.**

To investigate the effect of a change in mobility on the OLED light emission, "*ad hoc*" simulations are performed. After waiting for the system **to reach steady state**, the mobility of either electrons or holes is decreased by 1% for 1 μs and brought back to the starting value while monitoring the overall recombination. **Results are shown normalized in Fig. 2 *a* and *b*. Similarly to what is observed experimentally, there is a quench in the recombination that fully recovers once the mobility is restored to the equilibrium value. In the case of holes (*Fig. 2 b*) the recovery is not monotonic in contradiction with data in *Fig. 1*. Nevertheless such feature cannot exclude a hole mobility change since it depends strongly on the simulated layer thickness and the bias voltage and could not be visible in the experiment. A more quantitative model in which also the α-NPD layer is also taken into analysis is needed.** Looking at these results, it is possible to make some qualitative considerations. Besides the difference in magnitude and time response, strong voltage dependence **generally** characterizes the two cases. As the bias increases, both the rise time and decay time decrease, in contradiction to data shown in *Fig. 1*. This evidence suggests that the spin dependent process under examination directly affects the recombination rate and is independent of space charge reaction time which is bias dependent. Models that directly influence the recombination rate need to be taken into account [8, 16]. It should be noted that both electron and hole mobilities explicitly appear in the Langevin expression for the recombination rate (Eqn. 5). To explore the possibility that a change in carrier mobility could also affect the recombination rate *r(x,t)*, a more detailed microscopic model, which would also be dependent on the specific spin process, is needed. In the simulations reported in this paper, *r(x,t)* is kept constant. Simulations that take into account an instantaneous change in *r(x,t)* with carrier mobility were also performed (not shown here). **In this case the simulation output is quite different from what is shown in *Fig. 1* and *2* and changes significantly for electrons and holes. Overall a step like variation of the electroluminescence appears (reflecting the change in recombination rate) followed by a recovery overshoot that maintains a voltage dependence.**

5. Conclusions

Pulsed electromagnetic resonance detected by electroluminescence is used to characterize spin dependent processes in a Alq_3-based OLED. The time response of the device light emission to a high power resonant pulse shows very little dependence on the bias voltage. On the contrary, the time evolution resulting from a change in mobility should be strongly bias dependent as confirmed also by time dependent space charge limited current simulations. Hence, even though the effect of a magnetic field on the carrier mobility in Alq_3 has recently been proven, **it does not seem to be able** to account for the findings of this investigation. This suggests that spin dependent phenomena, acting directly on the recombination rate, play a relevant role in bipolar devices.

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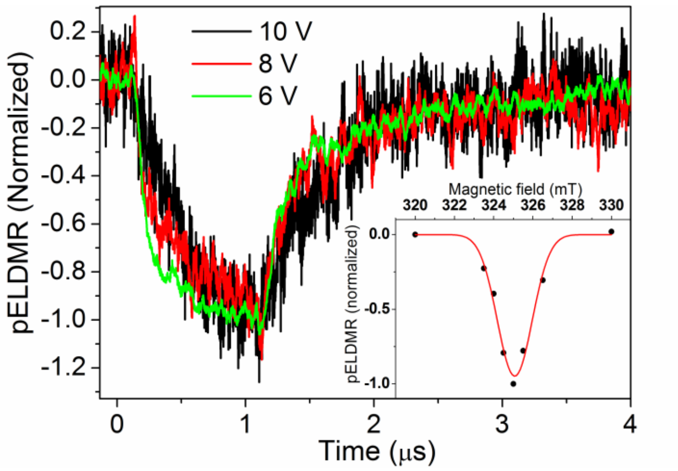

Fig. 1. Time resolved electroluminescence variation induced by a 1 μs MW resonant pulse at different bias voltages. The MW power used is of 30 W and the magnetic field is 325.2 mT. The inset shows the intensity of the electroluminescence variation versus magnetic field at 5.3 V fitted by a Gaussian. The intensity is calculated by integrating the electroluminescence variation in time domain. Data are normalized with respect to the maximum and the value at 320 mT is set as zero.

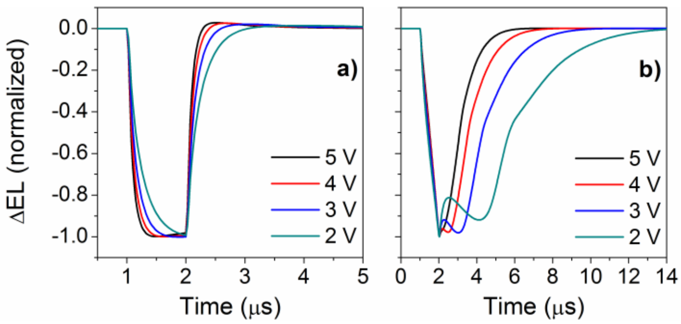

Fig. 2. Time profile of the electroluminescence variation calculated for a 1% change of electron mobility (a) and hole mobility (b) at different bias voltages. After 1 μs, the mobility is brought back to the initial value. All the mobility variations are performed gradually using a 50 ns ramp. All simulations are normalized for a better comparison with data in *Fig. 1*.