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# Charge Transport and Electroluminescence in PPV Mono- and Heterolayer Light Emitting Devices

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## ABSTRACT

Temperature dependent investigations of current-voltage and electroluminescence characteristics in mono- and heterolayer light emitting devices based on PPV and oxadiazole polymers between room temperature and 5K are reported. Electroluminescence quantum efficiencies in PPV LEDs can be largely increased by cooling or by the use of oxadiazole polymers. Transient EL measurements allow an estimation of hole mobilities in PPV and electron mobilities in the oxadiazole polymer.

## INTRODUCTION

Poly-Phenylene-Vinylene (PPV) was the first conjugated polymer where electroluminescence (EL) was observed.[1] Due to its good processability and high stability PPV and its derivatives are still attractive candidates as active materials for future organic electroluminescent display applications.
Monolayer light emitting devices (LEDs) from PPV usually show relatively low luminous efficiencies. These low values are a consequence of the fact that in PPV there is a strong imbalance of current flow for electrons and holes. It has been shown in measurements of current-voltage and capacitance-voltage characteristics that the p-type organic semiconductor PPV forms a Schottky contact with low work function metals like Ca or Al.[2] Electroluminescence in these devices is observed in forward bias direction (metal biased negative) at voltages exceeding values as low as 2V. However, since Schottky diodes are majority carrier devices, there is a large excess hole current, which does not recombine with the electrons injected at the metal electrode. Additionally, as a consequence of the inequality of the mobilities of electrons and holes, the recombination takes place near the polymer-metal contact, which possesses a large number of non-radiative pathways.
Beside the usage of metal-insulator-semiconductor (MIS) device structures[3] we have achieved an increase of external quantum efficiencies by using oxadiazole polymers[4] and small molecules[5] as an electron injecting/hole blocking layer between PPV and the metal electrode. External quantum efficiencies of 0.1% at a brightness of several hundred cd/m$^2$ have been achieved under driving conditions of about 100mA/cm$^2$ at 15V. In the following we will discuss temperature dependent investigations of I-V and EL characteristics, as well as transient experiments on PPV mono- and heterolayer LEDs, in order to give more insight into the physics of these devices. For shortness we will restrict ourselves here to one representative oxadiazole polyether (polymer **13** in the contribution of J. Bettenhausen et al. in these proceedings).

## TEMPERATURE DEPENDENCE OF DEVICE CHARACTERISTICS

We have investigated the current-voltage characteristics and electroluminescence light intensities of ITO/PPV/Al(Ca) monolayer LEDs and heterolayer LEDs with oxadiazoles as electron injecting layer (ITO/PPV/Oxadiazole/Al(Ca)) between room temperature and 5K.
Fig. 1 shows the corresponding curves for monolayer devices with Al as cathode material. At room temperature we observe the typical Schottky diode behaviour with a high rectification ratio of up to $10^6$, which has been described in several papers before.[2] With decreasing temperature the exponential rise of the current in forward direction (following the Shockley equation $I=I_S\{exp[e(V-IR_S)/nkT]-1\}$ between 1 and 4V) decreases and the I-V curves become more and more symmetric. The right plot in Fig. 1 shows the EL signals measured simultanously with the I-V curves. Parallel to the changes in the I-V characteristics we observe a significant increase of the onset voltage for EL. Whereas at room temperature EL occurs already below 2V for Ca electrodes, this threshold

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gradually increases upon lowering the temperature to reach values of more than 30V at 5K. Below about 200K the devices show EL also in reverse bias direction, however, with higher onset values. The observed temperature dependence can be explained by the transport properties of PPV. At room temperature PPV can be treated as a p-doped semiconductor forming a depletion layer at the Al (Ca) electrode with a width smaller than the total layer thickness.

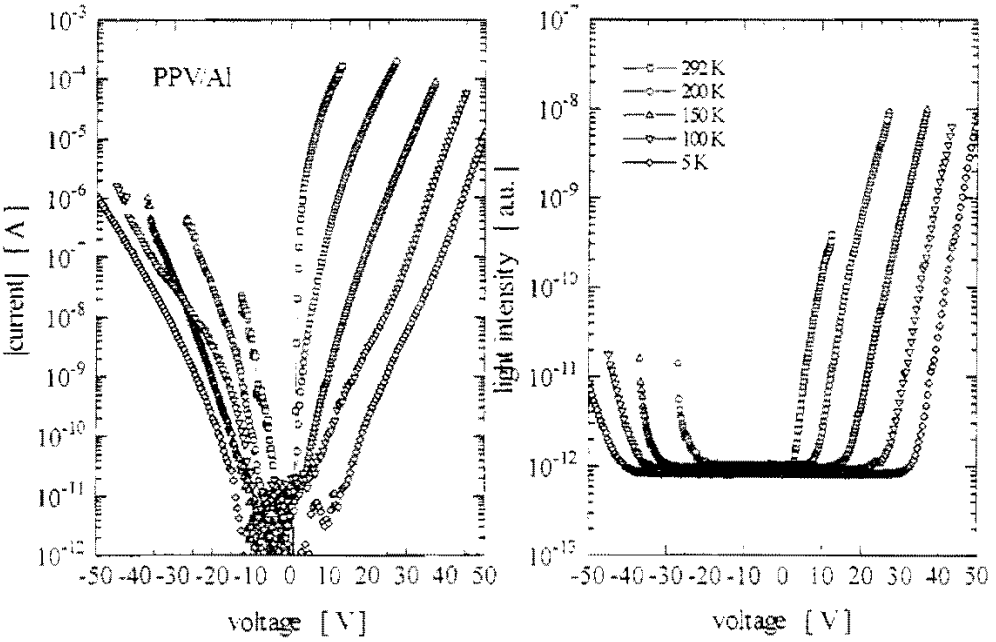


*Fig. 1: Temperature dependence of I-V and EL characteristics of ITO/PPV/Al LEDs (device area A=0.25cm² for all figures)*

Upon cooling the carriers gradually freeze out, which leads to an increase of the bulk resistance and the depletion layer width. At low temperatures the device is completely depleted and the device characteristics is essentially that of a metal-insulator-metal device. For this temperature range other injection mechanisms, such as Schottky, Poole-Frenkel, tunnel or field emission, have to be applied for a description of the observed behaviour. Additionally, the conduction at low temperatures is often limited by space charge effects. This is seen below 100K as a change in curvature of the I-V curves in forward bias direction, which coincides with the onset of EL. Since the appearance of EL indicates double injection, this behaviour is a strong indication for space charge limited currents.

In order to get information about the temperature dependence of the EL quantum efficiency it is useful to plot the light intensity versus current as shown in Fig. 2. It can be easily seen that the current density necessary for a certain fixed light intensity steadily decreases with lowering temperature. Consequently the EL quantum efficiency increases by two orders of magnitude between room temperature and 5K. From a typical value of 0.0003% at 300K, measured for ITO/PPV/Al with a calibrated detector, an external quantum efficiency of 0.03% at 5K can be derived. Remarkable is the fact, that all curves follow the same power law behaviour $I_{light} \propto I^B$ over almost four orders of magnitude with a temperature independent exponent B=1.3.

The observed strong temperature dependence of the quantum efficiency can be explained by the above mentioned transition from a p-type polymeric Schottky diode to a metal-insulator-metal device. We assume that the thermal freeze out of mobile charge carriers not only leads to an increase of the depletion layer at the Al electrode, but also to a formation of a hole barrier

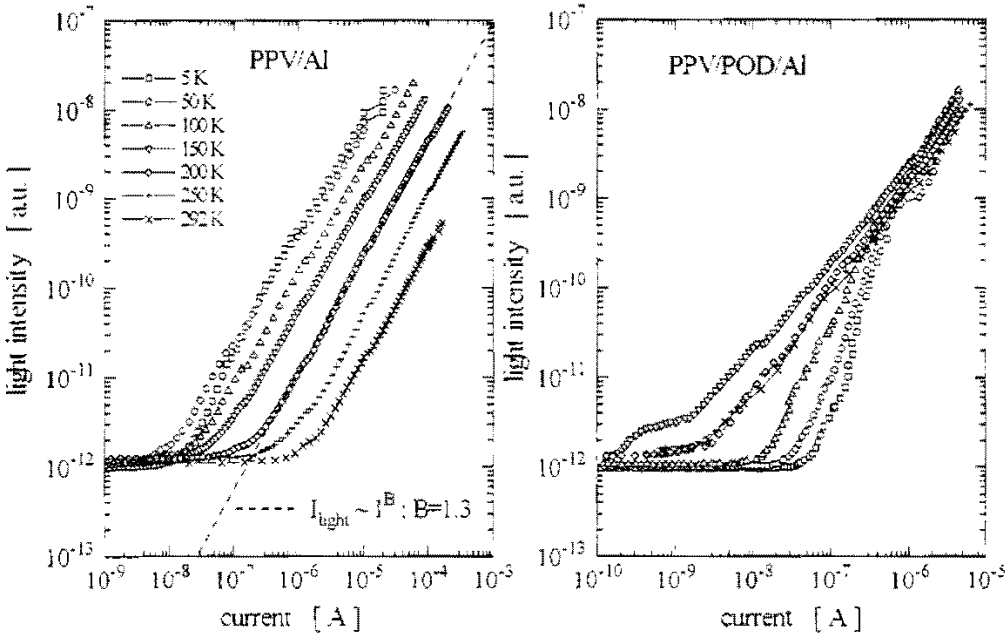


*Fig. 2: EL light intensity as a function of current for PPV monolayer and PPV oxadiazole polyether (POD) heterolayer LEDs*

at the ITO contact. Thus the injection of majority carriers (holes) is reduced, which leads to an improved charge balancing factor and consequently a higher quantum efficiency. Additionally, due to the larger depletion layer and the more balanced injection the recombination zone is shifted away from the immediate interface with Al into the polymer bulk, resulting in a reduction of non-radiative exciton quenching processes.

Analogous investigations of I-V and EL characteristics have been performed on ITO/PPV/Oxadiazole/Al(Ca) heterolayer devices. Apart from the fact that already at room temperature no Schottky diode behaviour and a much smaller rectification ratio ($10^3$) is observed, the overall temperature dependence of I-V and EL curves is qualitatively the same as for PPV monolayer LEDs. However, if one plots the EL light intensity versus the current, which is also shown in Fig. 2, and compares this to monolayer devices, significant differences are observed. For heterolayer LEDs a power law behaviour $I_{light} \propto I^B$ with B=1.2 is only observed down to 150K, at lower temperatures the EL at low currents depends even stronger on the current and leads into the same power law at higher currents. The most important difference concerning quantum efficiencies is that at room temperature the current necessary to achieve the same brightness is by two orders of magnitude lower in heterolayer devices. Thus already at room temperature external quantum efficiences of about 0.1% can be achieved.[4] In contrast to monolayer devices the maximum quantum efficiences in heterolayer LEDs, which are achieved at currents higher than $10^{-6}$A, are practically independent of temperature. This is also shown in Fig. 3, where we have compared the maximum achievable quantum efficiencies of mono- and heterolayer devices for Al and Ca electrodes. The plot clearly shows the already mentioned strong increase of quantum efficiencies by two orders of magnitude between 300 and 5K for monolayer LEDs and the temperature independence of this value for heterolayer devices.

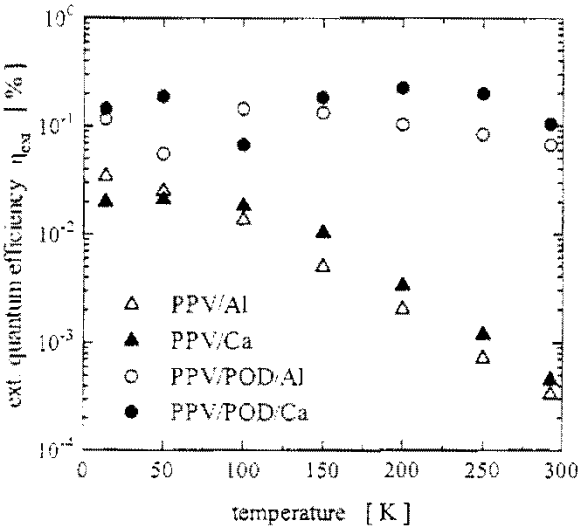


*Fig. 3: Temperature dependence of the maximum external quantum efficiencies in PPV mono- and heterolayer LEDs*

The above described behaviour and the enhanced quantum efficiency of heterolayer devices can be explained in an energy level diagram (Fig. 4). For simplification the p-doping of PPV is not included and only the ideal work functions are given, neglecting interfacial chemistry and interfacial layers. Though the value of the ionization potential (IP) and the electron affinity (EA) are not known exactly for the oxadiazole polyether, recent measurements of the LUMO level in solution via cyclic voltammetry (yielding $E_{LUMO}$=2.5eV) give strong evidence that the electron affinities of PPV and the oxadiazole are roughly the same. Thus the difference of the band gaps of the two materials leads to the formation of a hole barrier of about 0.6eV at the PPV/oxadiazole interface, which reduces the unipolar hole current flow and improves the charge balance. Additionally, this barrier leads to an accumulation of positive charge carriers at the PPV/oxadiazole interface, which can enhance electron injection. And finally, due to the electron transport capability of the oxadiazole, the recombination takes place at the polymer/polymer interface, which has much less non-radiative recombination centers.

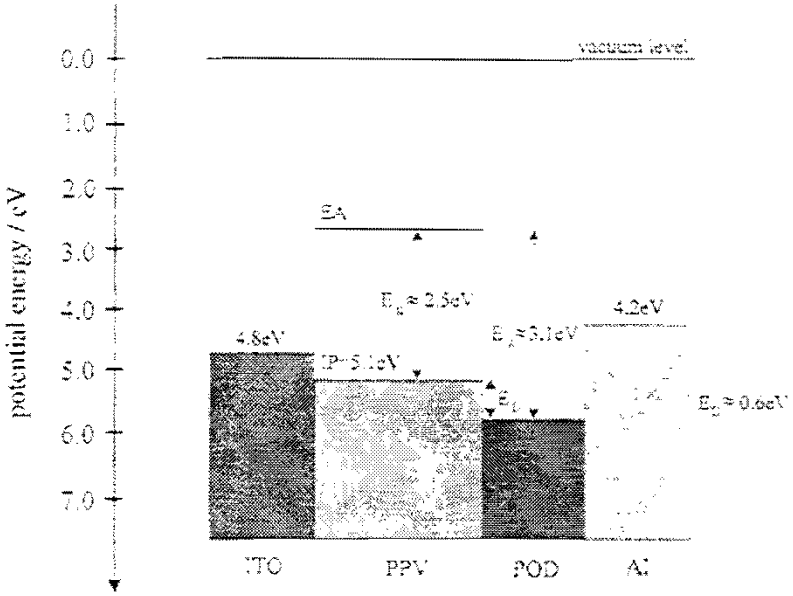


*Fig. 4: Energy level diagram of PPV/oxadiazole heterolayer LEDs*

## TRANSIENT ELECTROLUMINESCENCE

In order to get information about charge carrier mobilities we have performed transient electroluminescence measurements on PPV monolayer and PPV/oxadiazole heterolayer LEDs. Two representative curves for a 9V pulse excitation are shown in Fig. 5. In both cases there is a significant delay time between the application of the voltage pulse and the onset of EL. In PPV monolayer devices this delay time is due to the presence of a depletion layer at the Al contact. As the hole mobility in PPV is much larger than the electron mobility, this time lag corresponds to the time the holes need to pass the depletion layer (width 100nm) before they recombine radiatively with electrons. Therefore this value can be used to calculate an estimation for the hole mobility in PPV. Previous investigations have shown that the hole mobility varies exponentially (Poole-Frenkel detrapping model) with the applied bias and values between $10^{-7}$ and $10^{-5}$cm$^2$/Vs have been derived.[6] For the example shown in Fig. 5 we get a value of $\mu_h=10^{-5}$cm$^2$/Vs.

For heterolayer devices the delay time is about one order of magnitude larger at the same applied voltage. Due to the lower conductivity of the oxadiazole polymer, it is reasonable to assume that in heterolayer devices the applied voltage drops almost completely at the oxadiazole layer, which has a typical thickness of 50nm. In this case the time lag corresponds to the time the electrons need to cross the oxadiazole layer. Thus this measurement can be used to yield an estimate for the electron mobility in the oxadiazole polymer. Under the conditions shown in Fig. 5 we estimate the electron mobility to $\mu_e=10^{-7}$cm$^2$/Vs.

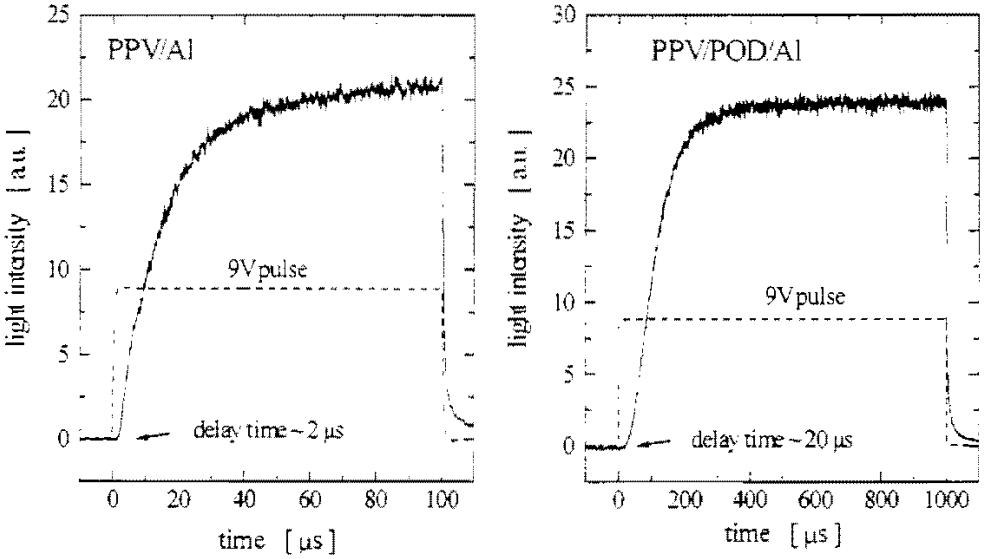


*Fig. 5: Transient electroluminescence in PPV mono- and heterolayer LEDs*

## CONCLUSION

PPV monolayer LEDs show a transition from a Schottky diode behaviour at room temperature to a metal-insulator-metal device behaviour at low temperatures. At the same time, the EL quantum efficiency increases by two orders of magnitude between 300 and 5K. The use of oxadiazole polymers as hole blocking and electron transport material in LEDs enhances the EL efficiency already at room temperature and values of 0.1% are achieved. From transient EL measurements the electron mobilities in the oxadiazole polymer are estimated to be about two orders of magnitude lower than hole mobilities in PPV. Thus, for further device improvement materials with better electron injection and transport properties have to be developed.

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