Full colour electroluminescence using dye-dispersed polymer blends

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Abstract

By blending suitable dyes into poly(N-vinylcarbazole) (PVK) we have fabricated devices which emit light in the whole visible spectrum. Their current–voltage (I–V) characteristics can be described by space-charge limited currents (SCLC) with effective trapping of the charge carriers by the dye molecules, while the light intensity shows a Fowler–Nordheim-like behaviour as a function of the mean electric field. We were able to model the electroluminescence characteristics by assuming tunnelling of the minority charge carriers through a triangular barrier. The obtained barrier heights showed a strong dependence on the dye molecules, suggesting that the injection of minority charge carriers takes place directly into the LUMO levels of the chromophors. The recombination along with the space charge leads to a steeper increase of the current and a Fowler–Nordheim-like I–V characteristic in the double injection regime though the majority carrier current is not injection-limited.

Keywords: Electroluminescence; Polymer blends; Dyes

1. Introduction

The use of molecular dyes is a widely used approach to the colour tuning of organic light-emitting devices (OLEDs). Emission over the whole visible range and also white light emission have been achieved [1–4]. The aim is to optimize separately the electrical and optical properties by suitable matrices and dyes. In this paper we present investigations of current–voltage (I–V) and brightness–voltage (B–V) characteristics showing that different dyes together with space-charge limited currents (SCLC) of holes have significant influence on electron injection.

2. Results and discussion

Several fluorescent dyes blended with poly(N-vinylcarbazole) (PVK) were investigated for their possible use in OLEDs (Fig. 1): low-molecular weight coumarine and methine dyes and a PVK-derived side chain polymer with a naphthalimide luminophore. The composition of the blends was 30/70 wt.% dye/PVK, except in the case of dye **2** with a dye content of only 15 wt.%. The polymer layers were sandwiched between indium–tin-oxide (ITO) and Al electrodes. Together with the blue emission of PVK the emission

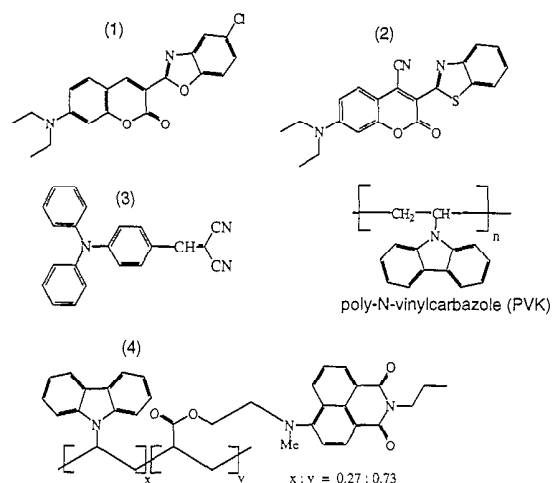* Corresponding author. Tel.: +49 921 552607; e-mail: wolfgang.bruetting@uni-bayreuth.de

Fig. 1. Fluorescent dyes (1–4) used in blends with PVK.

spectra of these dyes span the whole visible range as shown in Fig. 2. In Table 1 the corresponding CIE coordinates (x, y) are listed.

Fig. 3 shows the typical dependence of current and brightness on the applied voltage for thick polymer layers ($d \approx 300$ nm). At low bias voltage the I–V characteristic is symmetrical and can be described by a power law with an exponent between 4 and 7 depending on the dispersed dye. A kind of 'dephasing' between current and voltage can be observed for bias around zero, which depends on sweep direction
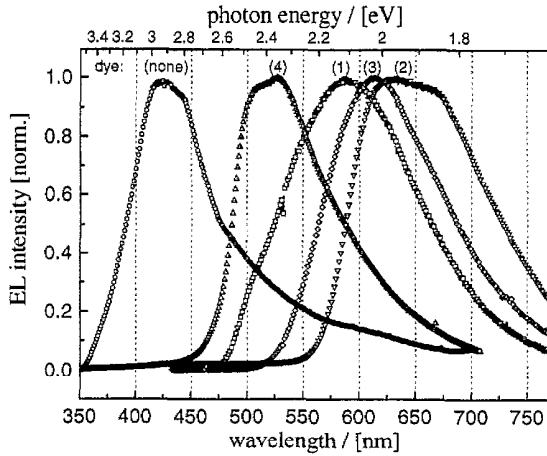
Fig. 2. Emission spectra of PVK and blend systems of PVK with dyes shown in Fig. 1.

Table 1
CIE coordinates of ITO/PVK + dye/Al devices

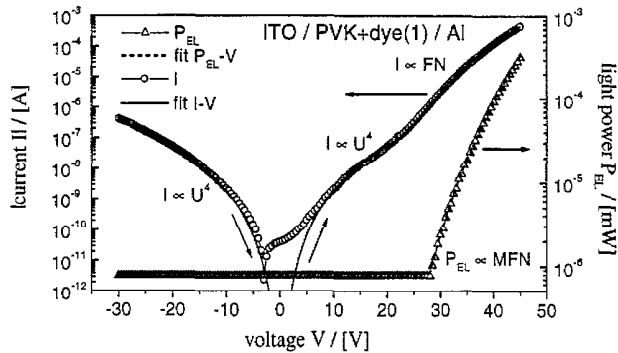| Dye	None	1	2	3	4
x	0.20	0.40	0.62	0.51	0.28
y	0.20	0.52	0.37	0.44	0.48
Colour	blue	yellow	red	orange	green

Fig. 3. Current–voltage and brightness–voltage characteristics of blend system PVK + dye 1. Film thickness 300 nm, active area 0.25 cm^2.

and speed. This can be explained in terms of trapped space charges near the injecting electrode.

At higher bias voltages ($V > 30$ V), when double injection and thus electroluminescence (EL) start, the characteristics show a rectification ratio up to 10^3 and higher. As the maximum (external) quantum efficiency of 0.05% photons per charge carrier is very low, even in the regime of double injection the current should be mainly constituted by holes (PVK is known as a hole transport material [5]).

Nevertheless, when electron injection starts the current increases much more steeply than in the case of single carrier injection. At high forward bias the current shows a Fowler–Nordheim (FN)-type behaviour. The solid line in Fig. 3 indicates the fit. In this case the current is much higher than for single carrier injection, though the current is still a majority carrier current. This behaviour can only be explained by the influence of electron injection and recombination along with

Table 2
Characteristics [a] of ITO/PVK + dye/Al devices

Dye	None	1	2	3	4
E_{onset} (10^5 V/cm)	16	7	6.5	8	20
η_{ext} max. (%)	6×10^{-3}	0.05	0.07	0.05	0.03
$\bar{\phi}_B$ (eV)	0.51	0.21	(0.21)	0.30	0.61

[a] E_{onset}: EL onset field, η_{ext}: ext. quantum efficiency, $\bar{\phi}_B$: eff. barrier height.

the space charge. Thus, the current flow is still bulk-limited. Therefore, the FN characteristics seen in the current cannot be attributed to an injection limitation via tunnelling of the majority carriers (holes).

Interestingly, the brightness–voltage characteristics also show an FN-type behaviour as indicated by the dashed line in Fig. 3. However, we will show below that the conventional FN law has to be modified due to the influence of the majority carrier space charge.

Generally, in these devices the onset voltage scales with the polymer layer thickness d and thus the device characteristics is field-dependent and not voltage-dependent. For the quantitative evaluation of our measurements we have chosen rather thick polymer layers, since the appearance of low voltage current anomalies (LVCAs) for d much below 100–200 nm causes considerable difficulties for the interpretation of the I–V characteristics. In a forthcoming paper we will show that these local unstable maxima in the current at low voltages do not influence the B–V characteristics. Hence the evaluation of the B–V dependence is possible also for thinner structures.

Furthermore, we observe an influence of the dye blended with PVK on the onset field (Table 2) and the exponent of the power law. Thus, the electrical properties of the polymer matrix and the dye cannot be separated — at least not at these high dye contents. When investigating the temperature dependence of EL we found only a slight change of the EL intensity with T. Therefore it is reasonable to assume that the injection of electrons will take place by tunnelling processes.

In the following the injection and transport of charge carriers will be discussed and a model will be proposed that enables us to describe the B–V characteristics. First of all we should discuss some general properties of SCLC. In the case of an exponential or Gaussian distribution of the energetic levels of traps or in the trap-free case, the I–V characteristic is given by a power law [6]:

$$I \propto V^{l+1}/d^{2l+1}$$

with $l = 1$ in the trap-free case and $l > 1$ otherwise. With the assumption of a spatially homogeneous trap distribution it is possible to calculate the electrical potential $\phi(x)$ and the electric field $E(x)$ within the device, where x designates the distance to the injecting electrode for majority carriers (anode):

$$\phi(x) = -V\left(\frac{x}{d}\right)^{\frac{2l+1}{l+1}}; \quad E(x) = \frac{2l+1}{l+1}\frac{V}{d}\left(\frac{x}{d}\right)^{\frac{l}{l+1}} \quad (1)$$
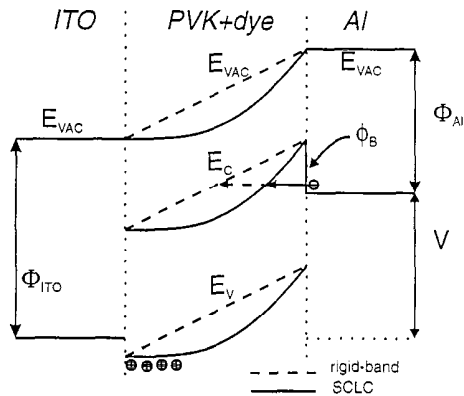
Fig. 4. Schematic energy diagram for electron injection in the presence of space charges.

Fig. 5. Fit of the modified Fowler–Nordheim Eq. (3) to brightness–voltage characteristics of devices with different thicknesses.

An important consequence of space charges is the fact that at the opposite electrode (cathode) the electric field is higher than the voltage V divided by the polymer thickness d: $E(d) = [(2l+1)/(l+1)](V/d) = \gamma(V/d) > (V/d)$. The field enhancement factor γ takes values in the range of 1.5–2. These values have to be interpreted with caution, because the interface between polymer and metal is not very well-known yet. However, it is obvious that the electric field at the minority carrier injecting electrode will be higher than the 'mean field' V/d, which has to be taken into account when describing electron tunnelling processes in these devices.

Our description of electron injection is based on the following assumptions: The light power is proportional to the electron current I_e and the electrons are injected via tunnelling at the cathode (FN) [7]:

$$P_{EL} \propto I_e \propto E^2 \exp\left(-\frac{2\alpha\phi_B^{3/2}}{3qE}\right) \qquad (2)$$

In the case of SCL hole current the electric field at the cathode is $E = \gamma V/d$ ($\gamma > 1$). With the definition of the mean field $\bar{E} = V/d$ and the effective barrier height $\bar{\phi}_B = \gamma^{-2/3}\phi_B$ ($\bar{\phi}_B \leq \phi_B$) one yields a modified FN law (MFN):

$$P_{EL} \propto \bar{E}^2 \exp\left(-\frac{2\alpha\bar{\phi}_B^{3/2}}{3q\bar{E}}\right) \qquad (3)$$

This equation is of the same form as the FN law; however, it does now contain the experimentally available mean field $\bar{E} = V/d$. The field enhancement factor γ cannot be determined directly because the electrical potential is changed slightly by the electron injection, which also influences the SCL current. Fig. 4 shows a schematic energy diagram with the potentials for the electrons (LUMO) and holes (HOMO). Compared to the rigid-band case the tunnelling
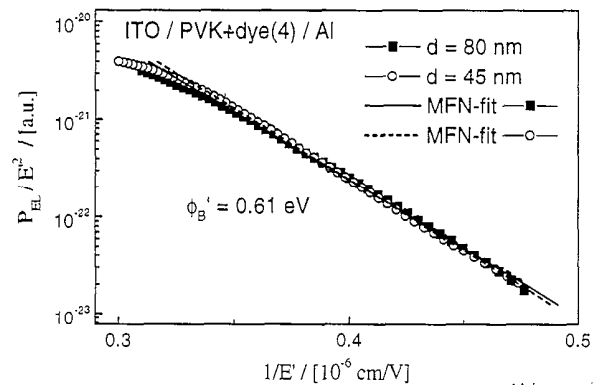
distance is reduced by the field enhancement at the cathode caused by SCLC.

According to Eq. (3) a plot of $\ln(P_{EL}/\bar{E}^2)$ versus $1/\bar{E}$ should give a straight line. From the slope the effective barrier height can be determined. In Fig. 5 the MFN plot for two different thicknesses is plotted. In both cases straight lines are obtained which are identical within the error of thickness measurement (5 nm). With Eq. (3) the B–V characteristics can be described very well over three orders of magnitude. In Table 2 the obtained effective barrier heights $\bar{\phi}_B$ for different dyes are given. They are strongly correlated to the EL onset fields, indicating that the limiting factor for EL is the electron injection in this case. The dependence of $\bar{\phi}_B$ on the dye suggests that electron injection takes place directly into the LUMO levels of the dye, which act as effective hole traps. Hence, not only the photoluminescence efficiency but also the LUMO levels of the dyes play an important role for EL — at least for high dye contents.

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