Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Initial Rise of Transient Electroluminescence in Organic Films

V. R. Nikitenko [a], A. R. Tameev [b] & A. V. Vannikov [b]

[a] Moscow Engineering Physics Institute (State University), Moscow, Russia

[b] A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of the RAS, Moscow, Russia

Version of record first published: 06 Jul 2012

To cite this article: V. R. Nikitenko, A. R. Tameev & A. V. Vannikov (2008): Initial Rise of Transient Electroluminescence in Organic Films, Molecular Crystals and Liquid Crystals, 496:1, 107-117

To link to this article: http://dx.doi.org/10.1080/15421400802451519

Mol. Cryst. Liq. Cryst., Vol. 496, pp. 107–117, 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802451519

Taylor & Francis
Taylor & Francis Group

Initial Rise of Transient Electroluminescence in Organic Films

V. R. Nikitenko[1], A. R. Tameev[2], and A. V. Vannikov[2]
[1]Moscow Engineering Physics Institute (State University), Moscow, Russia
[2]A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of the RAS, Moscow, Russia

Theoretical analysis of transient electroluminescence in thin organic films controlled by non-equilibrium charge transport is carried out including space-charge effects. Results are compared with experimental data for a 100-nm-thick film of a phenylenevinylene co-polymer. Normalized transients are highly dispersive and universal at the initial time interval, which is considered as a manifestation of the non-equilibrium field-assisted dispersion of holes. Transit time is the half-rise time rather than the delay time.

Keywords: field-assisted dispersion; organic light-emitting diodes; transit time

1. INTRODUCTION

The physical background of electroluminescence (EL) from thin organic films suitable for organic light-emitting diodes (OLEDs) was clarified greatly in the recent decade [1,2]. The zone of most intensive EL is typically a narrow (several nanometers) sheet in the proximity to one of the electrodes (a cathode, to be specific), due to a strong asymmetry of the mobilities of charge carriers [1,3]. The transport of fast carriers (holes, to be specific) across the almost whole layer is, consequently, a key process for the EL onset. Transient electroluminescence (TrEL) is widely considered as a general method for the determination of hole mobility in thin ($\leq$100 nm) organic films.

This work was financially supported by the RFBR (Projects 05–03–90579-HHC and 07-03-92112-GFEN) and NSC-RFBR (Joint Research Project 94WIA0100022).

Address correspondence to V. R. Nikitenko, Moscow Engineering Physics Institute (State University), 31, Kashirskoe Shosse, Moscow 115409, Russia. E-mail: vladronik@yandex.ru

Charge carrier transport in disordered organics occurs via hopping between localized states with a wide Gaussian energy distribution [4,5]. From studies of charge transport by conventional time-of-flight (TOF) techniques, it is well known that the initial non-equilibrium ("hot") energy distribution of excess charge carriers and the energy disorder of a material leads to anomalous characteristics of transport which are usually referred as dispersive transport. In particular, the anomalous broadening of carriers in space results in the anomalous broadening and scaling of normalized TOF signals, even if the signal is near-constant prior to the transit time [4]. However, the present methodology of TrEL analysis is typically based on the questionable assumption that the charge transport in thin ($\leq$100 nm) organic layers is normal, hence it can be described by constant mobility and diffusion coefficients, assuming also Einstein's relation [3,6]. The empirical method in [6] involves the dispersion of holes in a qualitative way, but it is not supported theoretically.

An analytic theory of anomalous (non-equilibrium) hopping charge transport has been developed recently in [7]. It is based on the concept of effective transport energy [8]. The transport is characterized by the time-dependent mobility and the coefficient of field-assisted diffusion. The latter describes an anomalous spatial broadening of charge carriers which is caused by the dispersion of release times of charge carriers from the deep tail of localized states. The theory includes the normal (quasiequilibrium) [9] and dispersive (extremely non-equilibrium) [10] regimes at long and short time ranges after the carrier generation, respectively. The TOF transients at the intermediate "quasidispersive" transport regime are in good agreement with the well-known results of experiments and Monte-Carlo simulations [4]. In work [11], the theory was applied to the modeling of the initial rise of TrEL from a single-layer OLED, providing the injection-limited transport of fast carriers (holes) in a device. The result is that a TrEL signal is anomalously broad due to the field-stimulated dispersion of holes incoming to the recombination zone.

In the present work, the model of [11] is developed in order to analyze effects of the space charge of holes and the slow transport of electrons on the initial rise of EL. Special attention is paid to the problem of correct determination of the mobility of holes from the TrEL data.

2. THEORY

TrEL is considered here providing that holes moves much faster than electrons, hence the recombination zone is located next to the cathode at the initial (after the switching-on of a voltage pulse at $t = 0$) time

period. The anode and the cathode are located at $x = 0$ and $x = L$, respectively, L is the film thickness. The recombination current density, $J_R(t)$ proportional to the TrEL intensity is the product of the conduction current density of holes, $J(L,t)$, incoming to the recombination zone, and the radiative recombination probability, $\varphi(t)$,

$$J_R(t) = J(L,t)\ \varphi(t). \tag{1}$$

The latter function increases with time (adiabatically slowly relative to the first one) due to (i) slow increase of the electron density and (ii) slow increase of the mean lifetime of singlet excitons because of the slow (dispersive) transport of electrons apart from the cathode. Therefore, the function $\varphi(t)$ is determined by rather complicated physical processes. It can be introduced, however, in a simple phenomenological way in order to reduce the number of model parameters. It is known that the TrEL kinetics shows often 2 different rise times which are related to the transport of electrons and holes, respectively [6]. Thus, one can write the function $\varphi(t)$ in this case as follows:

$$\varphi(t) \approx J_R(t)/J_R^{st} = 1 - (1 - \varphi_0)\exp(-t/\tau_e), \quad t \gg t_{tr}, \tag{2}$$

where t_{tr} is the transit time of holes, J_R^{st} is the long-time limit of $J_R(t)$, and $\varphi(t)$ is normalized by the condition $\varphi(\infty) = 1$, providing that the long-time TrEL kinetics can be described by the time τ_e, $\tau_e \gg t_{tr}$. One can obtain the parameter $\varphi_0 = \varphi(0) < 1$ by extrapolation of Eq. (2) to the zero time.

The time dependence of $J(L,t)$ is discussed at first, providing a rather high energy barrier for the injection of holes; hence, the electric field is uniform. One obtains [11]

$$J(L,t) = J_h\left(1 - \int_0^L dx p_\delta(x,t)\right), \tag{3}$$

where J_h is the injection current density of holes, and $p_\delta(x,t)$ is the distribution function of holes, being injected by a short pulse at $t = 0$ (see the analytic solution in [7,11]). It can be approximated by the Gaussian function, if $t \gg t_{eq\_\mu} \approx \nu_0^{-1}\exp\lfloor(\sigma/kT)^2\rfloor$, where ν_0 is the frequency prefactor, and σ is the variance of the Gaussian distribution of states:

$$\begin{aligned} p_\delta(x,t) &\approx \exp\left\{-(x - \mu_{eq}F_0 t)^2/4S_F(t,F_0)\right\}\Big/\sqrt{4\pi S_F(t,F_0)}, \\ S_F(t,F_0) &= \int_0^t dt' D_F(t',F_0). \end{aligned} \tag{4}$$

This function is characterized by the time-dependent coefficients of field-assisted diffusion (FAD), $D_F(t,F_0)$, and mobility $\mu(t) \approx \mu_{eq}$, $F_0 = (V - V_{bi})/L$ is the strength of the applied electric field, and V and V_{bi} are the applied and built-in voltages, respectively. Equations (3) and (4) yield

$$J(L,t) \approx J_h(1/2)erfc\left[(L - \mu_{eq}F_0 t)\Big/2\sqrt{S_F(t,F_0)}\right], \qquad t \gg t_{eq\_\mu}. \tag{5}$$

The quasiequilibrium transport regime is established at the long-time limit, $t \gg t_{eq-D}$, where $t_{eq-D} \approx \nu_0^{-1}\exp\left[2(\sigma/kT)^2\right]$: $D_F(t,F_0) \approx D_{Feq}(F_0)$ and $S_F(t) \approx D_{Feq}t$, although $D_{Feq}/\mu_{eq} \gg kT/e(\sigma/kT \gg 1)$ [7]. The FAD coefficient increases at the long intermediate period, $t_{eq\_\mu} \ll t \ll t_{eq\_D}$ ("quasidispersive" transport regime) [7,11]. The transit time of holes, t_{tr}, is determined by the condition that the mean position of the distribution of holes is equal to the film thickness,

$$\int_0^\infty dx x p_\delta(x,t_{tr}) = L, \tag{6}$$

in analogy with TOF. This condition yields $t_{tr} \approx L/\mu_{eq}F_0$ in the quasiequilibrium or quasidispersive regime, see Eqs. (4) and (5). Obviously, $t_{tr} \approx t_{1/2}$; see Eq. (5), where the half-rise time of TrEL, $t_{1/2}$, is defined as $J_R(t_{1/2}) = 0.5J_R(\infty)$.

If the space-charge limited regime of the hole transport is realized, the electric field strength, $F(x,t)$, is determined by the space charge of holes (except for several nanometers next to the cathode, where electron's charge is important), in accord with the Poisson equation. If the dispersive transport is finished, $t > t_{eq\_\mu}$, one can relate the current to the density of holes, $p(x,t)$:

$$J(x,t) \approx \mu(t)\exp[-\lambda(t)t]F(x,t)p(x,t). \tag{7}$$

The factor $\exp[-\lambda(t)t] \cong 1$ describes the capture on deep states ($\lambda(t)t \longrightarrow 0, t \longrightarrow \infty$). The functions $\lambda(t)$, $\mu(t)$, and $D_F(t)$ are determined by the energy σ and the temperature [11].

By neglecting the diffusion according to [12], the density of holes next to the cathode can be written as a step-like function,

$$p^{(0)}(x,t) = [\varepsilon\varepsilon_0/eM(t)]^l \int_0^{x_1(t)} dx_* \delta(x - x_*), \tag{8}$$

where $M(t) = \int_0^t dt'\ \mu(t')$, ε is the relative dielectric constant, and $x_1(t) = 2L\ln\{1/[1 - M(t)F_0/2L]\}$ is the leading front position. One can include approximately the field-stimulated broadening of a

step-like leading front of distribution (8), by replacing the Dirac delta-function in this equation by the Gaussian function (4), with x_* and $S_F[t, F(x_*, t)]$ instead of $\mu_{eq}F_0 t$ and $S_F(t, F_0)$, respectively. By using Eq. (7), we obtain

$$J(L,t) \approx \frac{\varepsilon\varepsilon_0\mu(t)}{2eM(t)}F(L,t)\exp[-\lambda(t)t]erfc\left[\frac{L - x_1(t)}{2\sqrt{S_F[t,F(L,t)]}}\right], \qquad t < t_1,$$

$$F(L,t) = F^{(0)}(L,t) - (e/\varepsilon\varepsilon_0)\int_L^\infty \left[p(x,t) - p^{(0)}(x,t)\right]dx,$$

$$\text{where } F^{(0)}(L,t) = F_0/[1 - M(t)F_0/2L] \tag{9}$$

The time t_1 is the transit time of holes in analogy with that in [12]; it is defined as $x_1(t_1) = L$, i.e.,

$$F_0 M(t_1)/L \approx 0.787. \tag{10}$$

Obviously, $t_1 \approx 0.787L/\mu_{eq}F_0$ [12], because $\mu(t) \approx \mu_{eq}$, if $t_1 \gg t_{eq\_\mu}$.

Equations (1), (2), and (9) [or Eq. (5) in the injection-limited regime] yield an approximate analytic description of the initial rise of TrEL. We note that the effects of the filling of deep states and the field dependence of the non-equilibrium mobility of holes are not considered here. Indeed, the calculations in [5,13] yield the weak dependence of the mobility on the hole density and the field strength, if $p/N \leq 10^{-4}$, $F_0 \leq 5 \cdot 10^5$ V/cm, $T > 250$ K, and $\sigma/kT \leq 3$, where N is the total concentration of states.

3. RESULTS AND DISCUSSION

Normalized TrEL signals calculated for the injection-limited (IL) and space charge limited (SCL) regimes of hole transport are shown in Figure 1 as dashed and solid curves, respectively. The calculations are carried out with the use of Equations (1) and (3) and (1), (2), and (9), respectively, for two values of applied voltage, 8 and 16 V. The film thickness is taken to be 100 nm, and the time is normalized by the half-rise time, $t_{1/2}$. The simplest case, $\varphi = const$, is assumed for the IL regime. The built-in voltage $V_{bi} = 2\,V$ is taken in account, so the field lies in the range from $6 \cdot 10^5$ to $14 \cdot 10^5$ V/cm. Figure 1 shows an approximate universality in both regimes. As the field increases, the dispersion parameter $W = (t_{1/2} - t_d)/t_{1/2}$ [11] varies from 0.64 to 0.76 and from 0.52 to 0.58 for the IL and SCL regimes, respectively. Obviously, TrEL rises steeper in the SCL regime. The delay times, t_d, are defined, as it is shown in Figure 1. Both these variations are much less than it is predicted by the conventional formula,

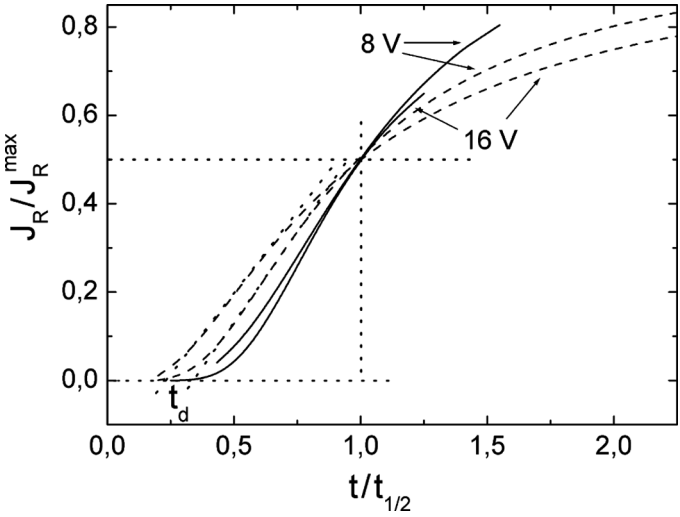

FIGURE 1 Time dependences of the initial rise of the recombination current calculated from Equations (1), (2), (9) (SCL regime, solid lines) and from Equations (1), (3) (IL regime, dashed lines). The recombination current and time are normalized by the steady-state level and by the half-rise time, respectively. Dotted lines show how the delay time is defined. Film thickness is $L = 100\,\text{nm}$, the built-in voltage $V_{\text{bi}} = 2\,\text{V}$. Other parameters: $\varphi_0 = 0.3$, $\tau_e = 3t_1$, where t_1 is calculated from Equation (10) (SCL regime); $\varphi(t) = \varphi_0$ (IL regime); $\sigma = 0.075\,eV$, $T = 295\,\text{K}$, $N = 4.6 \cdot 10^{21}\,\text{cm}^{-3}$, $2\gamma\, N^{-1/3} = 10$ (γ is the inverse localization length).

$W = \sqrt{\pi D/\mu F_0 L}$ [4], providing the time-independent FAD coefficient $D_{Feq} \propto F_0^2$ [9]. We note that both estimated transit times for the IL and SCL regimes [see Eqs. (6) and (10), respectively] considerably exceed the equilibration time of the mobility, t_{eq_μ}, hence the TrEL data are suitable for the determination of the mobility. However, an increase of the FAD coefficient in the long period, $t_{eq\_\mu} \ll t \ll t_{eq\_D}$, causes the normalized time dependences of the conduction current at the cathode, $J(L,t)$, to be approximately universal relative to variations of L and F_0 in analogy with the transient current under the TOF conditions [7,11] like the dispersive transport regime. If the Einstein's relation, $D/\mu = kT/e$, is the case, then one obtains a variation of W from 0.11 to 0.07 contrary to both the calculated and experimental (see below) results.

The results of calculations are compared with experimental data. Single-layer OLEDs were fabricated on ITO glass substrates covered with polyaniline (PANI) as a hole-injecting layer followed by a

100-nm-thick co-PPV layer as an active material, where co-PPV is poly[(p-phenylenevinylene)-alt-(2-methoxy-5(2-ethylhexyloxy)-p-phenylenevinylene)] from Sigma-Aldrich. The Ca cathode and the Al protecting layer were thermally deposited in vacuum. TrEL measurements were performed using a Keithley source-measure unit and a photomultiplier tube.

The built-in voltage for this structure is $V_{bi} = 2\,V$, and holes are the fastest charge carriers [14]. Figure 2 shows the semilogarithmic plot of experimental TrEL intensities, $J_{EL}(t)$, subtracted from its long-time value, $J_{EL}(\infty) = J_{EL}^{\max}$, and normalized by $J_{EL}^{\max}$. Obviously, the transit time can be determined by the method from [6] (see dashed lines), and this time is very close to the half-rise time of TrEL, $t_{1/2}$ (see also Fig. 13 in [6]). One can obtain the parameters of $\varphi(t)$, see Equation (2), from the long-time exponential asymptotics, namely $\varphi_0 \approx 0.3$ and $\tau_e(V = 10) = 2.2\ t_{1/2}$, $\tau_e(V = 16) = 2.7\ t_{1/2}$.

Figure 3 shows the universality of normalized TrEL intensities at the initial time period. The results are in good agreement with calculations for the IL regime (see the dashed lines), although the initial rise of experimental curves is somewhat steeper. Both calculated and experimental data are normalized to the steady-state level, and the time is normalized to the theoretical transit time of holes and the half-rise time, respectively. Again, one can identify the latter with

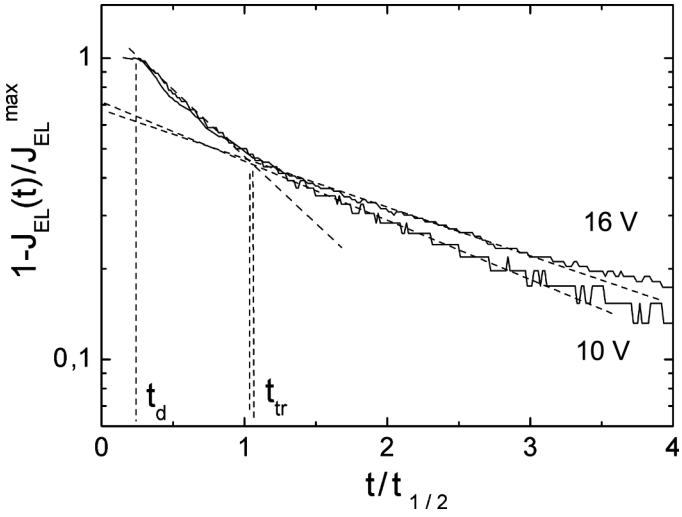

FIGURE 2 Normalized electroluminescence transients, obtained for the structure ITO:PANI/co-PPV (100 nm)/Ca:Al. Applied voltages are shown in the figure. Dashed lines show how the delay and transit times are defined.

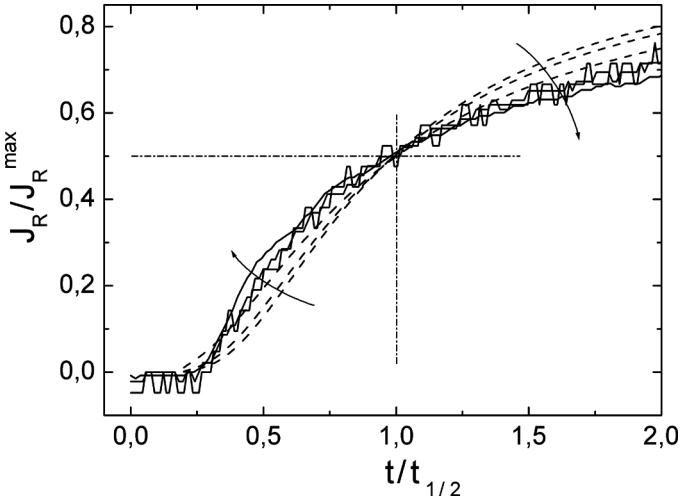

FIGURE 3 Normalized experimental TrEL signals (solid lines) compared with the recombination current calculated for the IL regime (dashed lines), see Equations (1), (3). Experimental and calculated curves are normalized by the half-rise time $t_{1/2}$ and the transit time t_{tr}, respectively. The latter is calculated from Equation (6) and coincides practically with $t_{1/2}$ Applied voltages are 8, 10, and 16 V, the increase is shown by arrows. Other parameters are the same as in Figure 1.

the transit time of holes, while the delay time of TrEL is much smaller than the transit time.

It is instructive to examine the possibility of non-equilibrium transport for the IL current. At the first glance, the initial energy distribution of injected charge carriers should be rather "cold" in order to preclude their subsequent energy relaxation, if the injection is barrier-limited. However, (i) localized states are shifted to lower energies next to the electrode by the one-dimensional image-force Coulomb potential and (ii) jumps downward in energy are possible due to the energy disorder. One can estimate [11] that the initial dispersive transport of holes is possible, if the energy barrier for the injection is rather low, $H < H_* = \sigma^2/kT + e^2/16\pi\varepsilon\varepsilon_0 a + eF_0 a$, where a is the typical hopping distance. If the injection occurs from the semiconducting anode, one has to replace ε by the effective value $\varepsilon_{eff} = \varepsilon(\varepsilon + \varepsilon_a)/(\varepsilon_a - \varepsilon)$ which is near ε for the typical case $\varepsilon_a \gg \varepsilon$, ε_a being the dielectric constant of the anode. For example, $H_* = 0.5\,\text{eV}$ at $\sigma = 0.075\,\text{eV}$ and $H_* = 0.7\,\text{eV}$ at $\sigma = 0.1\,\text{eV}$, providing that $a = 0.6\,\text{nm}$, $\varepsilon = 2.5$, and

$F_0 = 3 \cdot 10^5$ V/cm. It is worth noting that the quasidispersive transport regime is possible even if $H \geq H_*$ [11].

The difference of the work function of ITO and the HOMO level of co-PPV yields the energy barrier equal to 0.5 eV. The assumption about the IL- regime of hole transport is questionable, however, especially at the highest voltage. TrEL is calculated in the SCL regime for the same collection of parameters as that in Figure 3 and is compared with experiment in Figure 4. Obviously, the initial slope of the 16-V curve is reproduced by calculations better than that in Fig. 3. One can conclude that the transition from the IL to SCL regime of hole transport occurs with increase of the applied voltage from 10 to 16 V. The subsequent rise of the calculated curves is unreasonably steep, however, by suggesting that the accuracy of the approximate equation (9) is insufficient at $t \cong t_{tr}$. The steepness of the initial rise of TrEL in the SCL regime increases together with the electric field. The rise of TrEL is moderated, on the other hand, by the increase of $\varphi(t)$, which reflects the electron kinetics; hence, the calculated $t_{1/2}$ underestimates the transit time at low voltages not considerably.

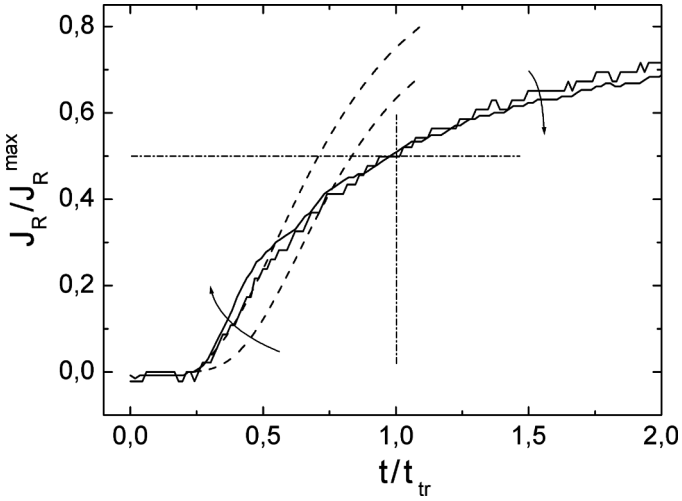

FIGURE 4 Normalized experimental TrEL signals (solid lines) compared with the recombination current calculated for the SCL regime (dashed lines), see Equations (1), (2), (9). $t_{tr} = t_{1/2}$ and $t_{tr} = t_1$, see Equation (10), for experimental and calculated curves, respectively. Applied voltages are 10 and 16 V, other parameters are the same as in Figure 1.

4. CONCLUSIONS

Effects of anomalous field-assisted dispersion on the initial TrEL kinetics cannot be ignored, basing on arguments following from both theoretical and experimental data. The transit time of the fastest charge carriers (holes) can be identified rather with the half- rise time of TrEL (in analogy with the half-decay time of TOF signals [4]), than with the delay time. The latter is a measure of the time-of-flight of the fastest fraction of holes whose hopping paths include only the states with energies shallower than the mean energy of occupied states in the quasiequilibrium regime, $-\sigma^2/kT$. One can overestimate the mobility (in the case of our experimental device, by a factor 4) if the delay time is taken as a transit time. The same conclusion was made in [6]. The method given in [6] is appropriate in our case as well (see Fig. 2). In general, the method of half-rise time seems to be more appropriate if the long-time TrEL kinetics is not pure exponential, and the steady-state level can be observed clearly.

The analysis performed in this paper can be not applicable to the case of the extremely high dispersion of TrEL signals, $W \geq 0.8$, in the SCL regime. The possible reasons are (i) *dispersive* (not quasidispersive) regime of hole transport and (ii) effects of electron transport on the initial TrEL [6]. The effect of charge accumulation on deep traps in the bulk of the film or in proximity to the electrodes [6,15,16] can be also important.

REFERENCES

[1] Friend, R. H., Gymer, R. W., Holmes, A. B., Burroughes, J. H., Marks, R. N., Taliani, C., Bradley, D. D. C., DosSantos, D. A., Bredas, J. L., Loglund, M., & Salaneck, W. R. (1999). *Nature*, *397*, 121.
[2] Blom, P. W. M. & Vissenberg, M. C. J. M. (2000). *Mater. Sci.*, *27*, 53.
[3] Crone, B. K., Campbell, I. H., Davids, P. S., Smith, D. L., Neef, C. J., & Ferraris. J. P. (1999). *J. Appl. Phys.*, *86*, 5767.
[4] Bässler, H. (1993). *Phys. Status Solidi B*, *175*, 15.
[5] Pasveer, W. F., Cottaar, J., Tanase, C., Coehoorn, R., Bobbert, P. A., Blom, P. W. M. de Leeuw, D. M., & Michels, M. A. J. (2005). *Phys. Rev. Lett., 94*, 206601.
[6] Pinner, D. J., Friend, R. H., & Tessler, N. (1999). *J. Appl. Phys.*, 86, 5116.
[7] Nikitenko, V. R., von Seggern, H., & Bässler, H. (2007). *J. Phys.: Condens. Matter*, *19*, 136210.
[8] Arkhipov, V. I., Emelianova, E. V., & Adriaenssens, G. J. (2001). *Phys. Rev. B*, *64*, 125125.
[9] Arkhipov, V. I. & Bässler, H. (1993). *Philos. Mag. Lett.*, *67*, 343.
[10] Arkhipov, V. I. & Bässler, H. (1993). *Philos. Mag. B*, *68*, 425.
[11] Nikitenko, V. R. & von Seggern, H. (2007). *J. Appl. Phys.*, *102*, 103708.
[12] Many, A. & Rakavy, G. (1962). *Phys. Rev.*, *126*, 1980.
[13] Arkhipov, V. I., Heremans, P., Emelianova, E. V., & Adriaenssens, G. J. (2001). *Appl. Phys. Lett.*, *79*, 4154.

[14] Scott, J. C., Malliaras, G. G., Chen, W. D., Breach, J. -C., Salem, J. R., & Brock, P. J. (1999). *Appl. Phys. Lett.*, *74*, 1510.
[15] Barth, S., Müller, P., Riel, H., Seidler, P. F., Riess, W., Vestweber, H., & Bässler, H. (2001). *J. Appl. Phys.*, *89*, 3711.
[16] Nikitenko, V. R., Tak, Y. H., & Bässler, H. (1998). *J. Appl. Phys.*, *84*, 2334.