Theoretical approach to kinetics of transient behaviour of Organic Light emitting diodes

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Abstract: *The present paper reports kinetics of transient behaviour of OLEDs on the basis of bimolecular recombination. An expression is derived for brightness of OLEDs and found to be increase quadratically with time and should attain saturation depending on current density. When voltage is turned off, the brightness should decay exponentially and then decrease following power law decay. The present study is helpful in determination of exciton lifetime, recombination coefficient and mobility of charge carriers.*

Keywords: exciton; bimolecular recombination; single layer device

Introduction

Organic and Polymer light emitting diodes (LED) are attracting a log of attention because of their potential for producing high conversion efficiency and high brightness materials for display applications. The high efficiency resulting form the effective recombination of oppositely charges carriers and high brightness due to the effective injection of both type of carriers can be obtained..

The transient behaviour of EL from OLED has attracted the attention of many workers because the pulsed excitation profile provides direct information on the dynamic processes leading to EL.. It has been reported by many workers [1-3] that in OLED bimolecular recombination of injected charge carriers takes place. However, when the number, of trapped charge carrier will be more than the number of free charge carries, then there is a possibility of monomolecular recombination. In the present paper, a theory based on bimolecular recombination. has been developed for the kinetics of transient behaviour of OLED.

2. Theory

In organic semiconductors, mostly the bimolecular recombination of charge carriers takes place. Some of the recombination's produce excitons and the rest of recombination's take place without the creation of excitons. If γ_1 is the rate constant for the bimolecular recombination producing excitons and γ_2 is the rate constant for the bimolecular recombination producing no excitons, then we can write the following rate equation.

$$\frac{dn}{dt} = g - \gamma_1 n^2 - \gamma_2 n^2$$

or,

$$\frac{dn}{dt} = g - \gamma n^2 \qquad (1)$$

where n is the number of charge carriers recombining in the emissive layer at any time t and $\gamma = (\gamma_1 + \gamma_2)$ is the recombination coefficient.

When a voltage-pulse is applied at t = 0, the EL emission takes place after a delay time of, t_d. As t_d is related to the transport of carriers to the emissive layer (EML), it can be assumed that the recombination of carriers will take place after, t_d, and we can take g = 0, at $t = t_d$. For this condition, the integration of eq. 1 gives

$$n = \sqrt{\frac{g}{\gamma}} \tan h \sqrt{g\gamma}\ (t - t_d) \qquad (2)$$

Thus, the rate of generation of excitons can be expressed as

$$G = \gamma_1 n^2$$

or,

$$G = \frac{\gamma_1 g}{\gamma} \tan h^2 \sqrt{g\gamma}\ (t - t_d) \qquad (3)$$

In bimolecular recombination's, the rate of generation of excitons is, $\gamma_1 n^2$, and the rate of recombination of charge carriers is, γn^2. Thus, the probability P_{ex}^m, of the formation of excitons during the bimolecular recombinations is given by

$$P_{ex}^b = \frac{\gamma_1}{\gamma} = \frac{\gamma_1}{(\gamma_1 + \gamma_2)} \qquad (4)$$

If δ_1 *and* δ_2 are the rate constants for the radiative and non-radiative decay of excitons, then we can write the following rate equation

$$\frac{dN_{ex}}{dt} = G - \delta_1 N_{ex} - \delta_2 N_{ex} \qquad (5)$$

where $\delta = (\delta_1 + \delta_2)$ and $1/\delta$ is the lifetime of excitons.

Transferring δN_{ex} on the right hand of eq. (5) to left hand side and them multiplying both the sides of the equation by $\exp[\delta(t - t_d)$ and as δ is the rate constant for the decay of excitons, it is a very big quantity of the order

$10^9\ s^{-1}$ and $\sqrt{g\gamma}$ $(\approx 10^6\ s^{-1}) << \delta$, therefore we get

$$N_{ex} = \frac{\gamma_1 g}{\gamma}\tanh^2\sqrt{gy}\,(t-t_d) + C\,\exp[-\delta(t-t_d)] \quad (5) \quad \text{or}$$

$$N_{ex} = \frac{\gamma_1 g}{\gamma}\tanh^2\sqrt{gy}\,(t-t_d) \quad (6)$$

As the radiative decay of excitons gives rise to the light emission, the photons emitted from a unit area of an OLED can be written as

$$\psi_{EL} = \delta_1 N_{ex} = \frac{\gamma_1 \delta_1 g}{\gamma\delta}\tanh^2(t-t_d) \quad (7)$$

For the OLED of thickness, d, and surface area, S. the number of photons emitted or the brightness of OLED can be written as

$$\phi_{EL} = \frac{Sd\gamma_1\delta_1 g}{\gamma\delta}\tanh^2[\sqrt{gy}(t-t_d)] \quad (8)$$

2.1 Rise of OLED Brightness

For low values of $(t-t_d)$, eq. (8) can be written as

$$\phi_{EL} = \frac{Sd\gamma_1\delta_1 g}{\gamma\delta}\left[\frac{1+\sqrt{gy}\,(t-t_d)-1+\sqrt{gy}\,(t-t_d)]}{1+\sqrt{gy}\,(t-t_d)+1-\sqrt{gy}\,(t-t_d)]}\right]^2$$

or,

$$\phi_{EL} = \frac{Sd\beta_1\delta_1 g}{\beta\delta)}\left[g\gamma(t-t_d)^2\right]$$

or,

$$\phi_{EL} = \frac{S\,d\,\beta_1\delta_1\,g^2}{\delta}(t-t_d)^2 \quad (9)$$

The above equation indicates that when the voltage will be applied to OLED, then initially ϕ_{EL} should increase quadratically with $(t-t_d)$. It is evident from eq. (8) that in bimolecular recombination's, ϕ_{EL} should attain a saturation value for larger values of $(t-t_d)$ and it is given by

$$\phi_{EL}^{sb} = \frac{Sd\beta_1\delta_1 g}{\gamma\delta}$$

or,

$$\phi_{EL}^{sb} = \frac{S\gamma_1\delta_1 J}{q\gamma\delta} \quad (10)$$

It is seen form eq. (10) that ϕ_{EL} is proportional to the injection current density, J. Although a linear relation has been found between ϕ_{EL} and J for certain OLEDs [4-6] in many cases nonlinear correlation has also been reported.. Thus, more accurately eq. (10) may be written as

$$\phi_{EL}^{sb} = \frac{H_0' S\gamma_1\delta_1 g^p}{q\,\gamma\delta} \quad (11)$$

where p is a power factor. And H_0' is a constant taking account of the inclusion of p in eq. (10).

Equation (10) indicates that the dependence of ϕ_{EL} on J should follow the power-type relation. It is to be noted that Kalinowski [2] and Riess[7] have reported experimentally the power-type relation between ϕ_{EL} and J, and thus, their results are in accordance with eq. (15).

2.3 Decay of OLED Brightness

When the applied voltage will be switched off at $t = t_c$, then g will become zero at $t = t_c$ and from eq. (1), we get

$$\frac{dn}{dt} = -\gamma n^2 \quad (12)$$

On Integration

$$\frac{1}{n} = \gamma t + C \quad (13)$$

where C is the constant of integration .

Equation (2) shows that for higher values of $(t_c - t_d)$, we can take $n = n_0 = (g/\gamma)^{1/2}$. Thus, taking $n = n_0$ at $t = t_c$, we get

$$C = \frac{1}{n_0} - \gamma t_c \quad (14)$$

From eqs. (13) and (14), we get

$$\frac{1}{n} = \gamma(t-t_c) + \frac{1}{n_0}$$

or,

$$n = \frac{n_0}{[n_0\gamma(t-t_c)+1]^2} \quad (15)$$

As discussed previously, the rate of generation, G, of excitons is equal to $\gamma_1 n^2$ Therefore, in the case of decay, we can write, $G = \gamma_1 n^2$. Thus, using eq. (15), we get

$$G = \frac{\gamma_1 n_0^2}{[n_0\gamma(t-t_c)+1]^2} \quad (16)$$

Now, the rate equation can be written as

$$\frac{dN_{ex}}{dt} = \frac{\gamma_1 n_0^2}{[n_0\gamma(t-t_c)+1]^2} - \delta N_{ex} \quad (17)$$

Multiplying both the sides by $\exp[\delta(t-t_c)]$, we get

$$dN_{ex}\exp[\delta(t-t_c)] + \delta N_{ex}\exp[\delta(t-t_c)] = \frac{\gamma_1 n_{0\exp[\delta(t-t_c)]}^2}{[n_0\gamma(t-t_c)+1]^2} \quad (18)$$

As the lifetime of excitons is very short, δ is large, and therefore, eq. (14) may be approximated as

$$N_{ex}\exp[\delta(t-t_c)] = \gamma_1 n_0^2\frac{\exp[\delta(t-t_c)]}{\delta}.[n_0\gamma(t-t_c)+1]^{-2} + D \quad (19)$$

For $t = t_c$, $N_{ex} = N_{ex}^0$, [$= \gamma_1 g/\gamma\delta$, from eq. (6)], hence, eq. (19) gives

$$N_{ex}^0 = \frac{\gamma_1 n_0^2}{\delta} + D$$

Or,

$$D = N_{ex}^{0} - \frac{\gamma_1 n_0^2}{\delta} \qquad (20)$$

Thus, from, eqs. (19) and (20), we get

$$N_{ex} = \frac{\gamma_1 n_0^2}{\delta[n_0 \gamma (t-t_c)+1]^2} + \left(N_{ex}^{0} - \frac{\gamma n_0^2}{\delta} \right) \exp[\delta(t-t_c)] \qquad (21)$$

Now, the following two cases arise

Case I : Small Values of $(t - t_c)$

For small values of $(t-t_c)$, eq. (21) may be approximated as

$$N_{ex} = N_{ex}^{0} \exp[\delta(t-t_c)] \qquad (22)$$

Thus, the decay of OLED brightness can be expressed as

$$\phi_{EL} = S d \delta_1 N_{ex}$$

or,

$$\phi_{EL} = S d \delta_1 N_{ex}^{0} \exp[-\delta(t-t_c)] \qquad (23)$$

$$\left(\text{as } S d \delta_1 N_{ex}^{0} = S d \delta_1 \gamma_1 . n_0^2 = \frac{S d \gamma_1 \delta_1 g}{\gamma \delta} \right)$$

Equation (23) indicates that for smaller values of $(t-t_c)$, the EL brightness should decay exponentially where the decay time will be equal to $1/\delta$. Thus, by measuring the initial decay of EL brightness, the lifetime $(1/\delta)$ of excitons can be determined.

Case II: Large, for larger values of $(t-t_c)$

As $\delta$is large, for larger values of$(t-t_c)$, the second term in eq. (21) can be neglected. Thus, we get

$$N_{ex} = \frac{\gamma_1 n_0^2}{\delta[n_0 \gamma (t-t_c)+1]^2} \qquad (24)$$

Now, the decay of EL brightness can be expressed as

$$\phi_{EL} = \frac{S d \gamma_1 \delta_1 n_0^2}{\delta[n_0 \gamma (t-t_c)+1]^2} \qquad (25)$$

For $n_0 \gamma (t - t_c) >> 1$, $\phi_{EL} = \dfrac{\phi_{EL}^{sb}}{n_0^2 \gamma^2 (t-t_c)}$ (26)

where, $\phi_{EL}^{sb} = \dfrac{S d \gamma_1 \delta_1 n_0^2}{\delta}$ is the value of ϕ_{EL} at $(t-t_c)$

Equation (26) indicates that for larger values of $(t-t_c)$, ϕ_{EL} should decrease following power law decay.

3. Conclusions

The theoretical analysis confirms that the light emission from OLEDS takes place due to the radiative decay of singlet excitons produced during the bimolecular recombination of oppositely charged carriers injected from electrodes.. The present study of transient behavior of single and multilayer OLEDs helps in determination of exciton lifetime, recombination coefficient and mobility of charge carriers and there is good correlation between experimental and theoretical results

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