Organic Electronics 14 (2013) 3117–3122

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Transient luminescence in organic light-emitting diodes explained by trap-assisted recombination of stored charges

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ARTICLE INFO

Article history:
Received 22 March 2013
Received in revised form 18 July 2013
Accepted 18 July 2013
Available online 6 August 2013

Keywords:
OLED
Delayed electroluminescence
Transient electroluminescence
Recombination
Trapping
Trap assisted recombination

ABSTRACT

We show that after voltage turn-off the recombination of the charges which are stored in the on-state may follow a trap-assisted mechanism instead of the Langevin formula in organic light-emitting diodes. A microscopic model based on this form of recombination is introduced, which not only fits the transient electroluminescence very well in the whole range of the off-state but also provides parameters quantitatively characterizing the stored charges in the on-state. In the last part, we briefly compare the work by Weichsel et al. [1] and our model, trying to constitute a comprehensive picture of the stored charges in OLEDs. As an OLED model system we have chosen a host/guest system co-doped with red and green phosphorescent emitters.

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1. Introduction

Organic light-emitting diodes (OLEDs) have gained huge attention from academic research and from industry. Despite their already excellent properties, the lifetime and efficiency still need improvement, since especially general lighting applications ask for high brightness. One of the concerns is the charge-storage within the device, which is generally believed to have impact on the efficiency and degradation of devices [2–4]. To improve the devices, a better understanding of the relevant physical processes in the emission zone is required. Transient electroluminescence (transient EL) proves to be a useful tool to investigate the processes within emitting layer (EML) of OLEDs, since the luminescence is proportional to the concentration of excitons [5,6]. In phosphorescent OLEDs, the intrinsic decay of triplets after voltage turn-off follows the expression $X(t) = X^* e^{-t/t_i}$, where $t_i = 1/k_i$ is the lifetime of triplets. The asterisk here and in the following part of this paper denotes that the corresponding term is a quantity in the on-state (steady state). Besides intrinsic radiative decay, complex processes influence the transient EL in the off-state, and one of these processes is the recombination of the stored charges within EML [1,7–10]. When we examine the phenomena in transient EL related to those stored charges we find that they can be categorized into two effects: one is an "over-shoot" of the bipolar (switching the applied voltage to negative values after excitation) transient EL signal [1,7–10] and the other is the recombination-induced luminescence ("long tail" of the EL signal) [8,9]. Weichsel et al. [1] recently reported that the "over-shoot" in bipolar transient EL of phosphorescent OLEDs originates from the accelerated recombination of charges accumulated at the boundary of EML; while earlier, Cheon and Shinar [9] attributed the "over-shoot" to the recombination of correlated charge pairs and attributed the long tail to uncorrelated charges, and used a function of $1/t$ behavior to describe the process of charge-recombination based on Langevin recombination formula [11].

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http://dx.doi.org/10.1016/j.orgel.2013.07.022

2. Theory

We start our study from the rate equation of triplet-concentration after voltage turn-off considering the contribution from recombination of stored charges. In the off-state, the loss processes [12] as triplet–triplet annihilation (TTA) and triplet-polaron annihilation (TPA) are neglected due to the fast consumption of triplets. With proper confinement of triplets by choosing materials with high triplet levels in layers neighboring to EML, the energy transfer to triplets in the neighboring layers can be effectively avoided. Therefore the generation and quenching of triplets in EML after turn-off follow the two pathways respectively.

$$n + p \rightarrow X \tag{1}$$

$$X \rightarrow \hbar\omega \tag{2}$$

The rate equation of triplets in the off-state, when charges are taken into account, reads as

$$\frac{dX(t)}{dt} = -k_i X(t) - \frac{dQ(t)}{dt}, \tag{3}$$

where $X(t)$ and $Q(t)$ denote the concentration of triplets and stored charges participating the radiative recombination within EML respectively. We shall show in the later part of this paper that what we are discussing is a type of recombination between mobile charges and trapped charges, and one stored charge corresponds to one triplet within the period of time we are considering, thus the proportionality of dX/dt to dQ/dt always holds. To solve Eq. (3), one needs to know the expression of $Q(t)$. In previous works, Langevin formula has been widely used for describing the recombination in OLEDs [8,13,14], and the validity of it in OLEDs has been studied by simulation methods [15,16]. However, those works deal with the recombination in the on-state when most of the charges are mobile charges, i.e. electrons in the LUMO level and holes in HOMO level. When trapping effects become more pronounced, the Langevin formula may be not valid [17,18]. For such a situation, a trap-assisted recombination formula was recently introduced to describe the behavior of the charges in disordered organic semiconductors [18]. Trap-assisted recombination, also known as SRH recombination [19,20], was commonly regarded as a non-radiative process because it requires the participation of phonons to fulfill the conservation of momentum. However, Wetzelaer et al. reported that in white-emitting copolymer where green and red-emitting chromophores are incorporated in the blue-emitting polyfluorene backbone [21,22] the trap assisted recombination can contribute to radiative emission instead of being a loss mechanism for luminescence as generally regarded [17].

The trap-assisted recombination is a two-step process. In the first step, each neutral trap within EML captures an electron from the LUMO (or a hole from the HOMO), and in the second step, a hole from HOMO (or an electron from LUMO) is captured, forming an exciton. (Fig. 1) In other words, the trap-assisted recombination is the recombination of a mobile charge and a trapped charge. In on-state, capturing happens far more frequently than emission, so that the traps are occupied again immediately after recombination or emission happens, thus the recombination rate equals the net capturing rate [19].

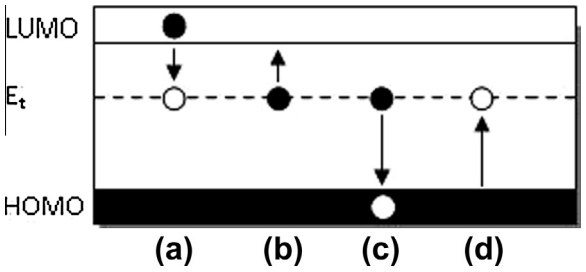

Fig. 1. Schematic representation of trap-assisted recombination [19]: (a) electron capture, (b) electron emission, (c) hole capture, and (d) hole emission.

Now we apply the trap-assisted recombination to the turn-off dynamics. The used symbols are listed in Table 1.

After voltage turn-off, the amount of mobile charges within EML is no longer constant. Therefore the off-state is a non-steady state in which the carrier statistics is quite different from that in the on-state. Nevertheless, in a short period of time after turning off, the amount of mobile charges is still large enough compared with its change so that a quasi-steady state where net capturing rate for each trap is still equal to the recombination rate as in the on-state is maintained. This quasi-steady state lasts for a certain while until the decrease of the amount of mobile charges is no longer negligible. Now, the recombination rate is no longer the net capturing rate as it is in the quasi-steady state because of the formation of empty traps. Instead, the recombination rate in the later state is the rate of capturing two opposite mobile charges at an empty trap, which is much smaller than previously in the quasi-steady state. For this reason, one would expect that the luminescence in the off-state is mainly caused by the processes which happen in the quasi-steady state shortly after turning off and suggest that the quasi-steady state approximation is valid for studying the processes responsible for the recombination-induced luminescence after voltage turn-off. In the following part, we base our discussion therefore on the quasi-steady state approximation.

According to Ref. [19], and quasi-steady state approximation, the total recombination rate in the off-state then reads as

$$R = U_{cn} + U_{cp} \tag{4}$$

$$U_{cn} = N_{tp} C_n n - N_{tn} C_n n e^{(E_t - E_{Fn})/k_B T} \tag{5}$$

$$U_{cp} = N_{tn} C_p p - N_{tp} C_p p e^{(E_{Fp} - E_t)/k_B T} \tag{6}$$

The second term in the right side of Eq. (5) relates to electron emission (process (b) in Fig. 1) according to Eq (3.2) and Eq. (3.7) of Ref. [19], and is negligible when E_t is far below the quasi-Fermi level for electrons as in the case of our devices. Further, $C_p = \mu_p q/\varepsilon$ and $C_n = \mu_n q/\varepsilon$ hold according to Ref. [18]. In our devices, holes which do not participate in forming triplets tend to be trapped whereas the excessive electrons are stored in a mobile state

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