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Simultaneous and direct measurement of carrier diffusion constant and mobility in organic semiconductors and deviation from standard Einstein relation

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We show that the shape of electroluminescence transients in organic semiconductors can be conveniently used to obtain the diffusion constant D of injected charge carriers, enabling the study of generalized Einstein relationship under nonequilibrium conditions as a function of the electric field. The appearance of peak at the onset of transient is shown to be the signature of diffusive regime of transport. We demonstrate it for two representative materials, $\mathrm{Alq_3}$ and polymer poly [2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene], with the focus on the role of hot carriers in transport and their diffusivity.

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The emergence of organic and polymeric semiconductors[1] as electronic materials has brought to focus the need for a deeper understanding of the carrier drift-diffusion equations.[2,3] In most applications of organic semiconductors, the carrier statistics are considered as degenerate[4] from this perspective and hence, the need to invoke the generalized Einstein relationship $D/\mu = \chi(k_BT/q)$, where the factor χ is a thermodynamic factor and is defined as $\chi = (n/k_BT)(\partial\eta/\partial n)$, where n is the carrier concentration and η is the chemical potential. The thermodynamic factor χ is thus a measure of the extent of deviation from the standard nondegenerate Einstein relation.[2,4–7] The theoretical motivation to understand abnormal diffusivity in hopping controlled regimes has traditionally come from the anomalous broadening of time-of-flight (TOF) signals[2,8] despite the occurrence of well-defined plateaus, and more recently, a broadening in switch-on electroluminescence transients (ELT),[9] and ideality factors of organic junction diodes.[10,11] This has led to a quest for a deeper understanding of transport in disordered solids, in general, as provoked by the early studies of Richert *et al.*[2] and their current resurgence.[12–14] There have been attempts to measure χ in organic solids using techniques such as photoelectromotive force measurements[15] and Kelvin force measurements.[16] However, these techniques do not measure the diffusion constant D for the study of deviation from the standard Einstein relationship. Traditionally D is sought to be derived from TOF experiments,[17] however, the procedures seem to be indirect and require specific samples and conditions. In this Rapid Communication we show that for typical injection conditions and high fields used in applications, the transport of carriers displays a diffusive regime during transport enabling the direct measurement of D and mobility μ, and we demonstrate it for two prototypical organic materials.

We use the ELT technique in which a voltage pulse injects a bunch of carriers which move toward the opposite electrode to meet the carriers from the other electrode to recombine and give out luminescence. The measured time difference between the application of the voltage step and the appearance of light is the duration of the drift of carriers under a known average applied electric field, and hence allows the determination of μ. The mobility of the fast carriers is usually measured in such an experiment since the slower of the carriers has mobility typically lower by several orders.[18] The onset of electroluminescence (EL) is normally observed to be broad[4,9] and has been attributed to dispersive transport in which carriers relax in energy during transit giving rise to a broad velocity distribution. However, despite some attempts, a satisfactory model of the broadening, which can be used to obtain transport parameters of interest, does not exist. Nikitenko *et al.* have suggested that the broadening of onset in ELT is due to field-induced dispersion.[9] In this work, we focus on a more intriguing feature of ELT in which a distinct peak occurs at the switch-on edge. Though this phenomenon has been reported by several authors,[19–21] it has not been explained cogently and quantitatively, and is considered as a challenge to modeling.[22] In this study we show that the appearance of the peak is due to a combined effect of drift and diffusion of a packet of carriers. This is reminiscent of the way minority carriers in inorganic semiconductors were studied in the well-known Haynes-Shockley experiment.[23]

We use two well-characterized organic luminescent semiconductors viz. small molecule tris(8-hydroxyquinolinolato) aluminum (III) ($\mathrm{Alq_3}$) and polymer poly [2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), respectively, in a sandwich device configuration. The RCA cleaned indium tin oxide (ITO as anode) substrates were pretreated under oxygen-argon plasma prior to active layer deposition. The small molecule device fabrication was carried out in a state-of-the art automated multichamber vacuum-deposition system. A hole injecting layer of 4,4′,4″-tris[*N*-(3-methylphenyl)-*N*-phenylamino] triphenylamine (m-MTDATA) doped with tetrafluoro-tetracyano-quinodimethane ($\mathrm{F_4}$-TCNQ) is deposited followed by the $\mathrm{Alq_3}$ layer resulting in a device structure ITO/m-MTADTA/$\mathrm{Alq_3}$/LiF/Al. The single layer MEH-PPV diode (ITO/PEDOT:PSS/MEH-PPV/cathode) is fabricated with two different cathodes (calcium and aluminum) for comparison. MEH-PPV was spin cast in a nitrogen glovebox from solution prepared in xylene:chloroform (50:50). The thickness of the active layer was determined using a profilometer (Tencor alpha–Step 500). For ELT measurement, a 50 MHz HP 81101A pulse generator (rise time 10 ns) was used to apply rectangular voltage pulses of different magnitudes across the device. A photomultiplier tube (S100 response with time resolution <1 ns), facing the

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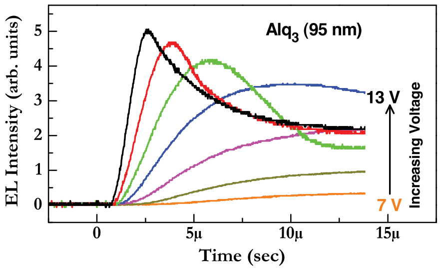

FIG. 1. (Color online) ELT response of Alq$_3$/LiF/Al device in steps of 1 V. Note that EL overshoot is observed for higher voltages.

emitting area of the device, was connected to a 500 MHz digital oscilloscope (model HP 54615B) to record the time-dependent electroluminescence signals. The details of the ELT measurement procedure have already been reported elsewhere.[18]

Figure 1 shows a set of EL transient curves for Alq$_3$ devices for different magnitudes of voltage pulse. In this case a packet of electrons is injected which drifts toward the *p*-doped m-MTDATA and recombines at the interface giving rise to ELT. For lower voltages, the usual broad onset due to field-induced dispersion[9] is observed. However, beyond a certain voltage, the onset becomes sharp and a peak is observed, as shown in the figure. On increasing the voltage further, the peak becomes narrower and moves to a shorter time.

Figure 2 shows two sets of EL transients for MEH-PPV devices with two different cathodes. For the case of the Ca cathode [Fig. 2(a)], the dominant feature is the appearance of an ELT peak which becomes successively narrower at higher voltages. In contrast, with Al acting as the cathode, and all other conditions of the device preparation remaining the same, the striking feature of the peak is absent in a similar set of curves, as shown in Fig. 2(b). This shows that the injection of copious electrons at the cathode is necessary for the appearance of the peak. We have recently shown that in such MEH-PPV devices,[18] for lower electric fields the mobility is controlled by electrons. However, for higher fields, especially in the range where the peak is observed as shown here, the effective mobility is dominantly due to injected holes. This has been explained on the basis that at higher electric fields, the local density of states get so severely misaligned that injected electrons do not find overlapping transport states in the adjoining layers. They are forced to relax, producing a large and sharp electron profile at the MEH-PPV/Ca interface. Hence the observation of the peak is due to the profile of injected holes arriving at the cathode recombining there with the much larger concentration of electrons. There have been differing perspectives in the literature on the role of electrons as a mobile species in MEH-PPV/Ca devices.[24] We have argued in Ref. 18 that for the case of a low work-function Ca cathode, electrons are injected directly into the transport states and the transient constitutes its transport before it can relax at low electric fields. At lower voltages, when hole injection is inadequate, the EL signal rises to the level of steady state displaying only a broadened onset customarily attributed to field-induced dispersion.[4,9,12]

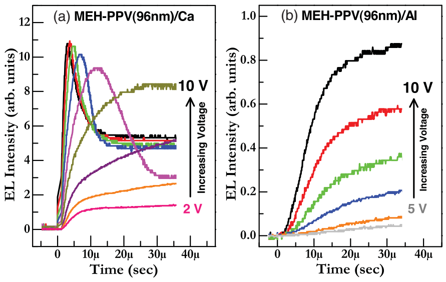

FIG. 2. (Color online) ELT response of single layer diode for two different cathodes (a) MEH-PPV/Ca and (b) MEH-PPV/Al devices in steps of 1 V. Note that for the case of the Ca cathode, an overshoot in intensity is observed at switch-on of voltage pulse while no overshoot occurs in the case of the Al cathode device.

Our analysis depends on the observation that the ELT shape is a reflection of the profiles of the moving charge packets when they meet each other initially, before settling down to steady-state profile, consistent with space-charge-limited current. The analysis is particularly simple and informative if one of the moving species is fast and arrives at a sharp recombination front. When the injected carriers in the initial leading edge are more than the steady-state levels, the excess carriers diffuse away from the leading front which acts as the source of carriers for back diffusion. The shape of the transient is controlled by the rate-limiting species, and the supply of the other carrier for recombination is considered to be nearly constant for the duration of the pulse, an assumption valid in most cases due to highly asymmetrical values of mobility of carriers with opposite charges. It is important to emphasize that once the peak appears the onset is sharp, becoming progressively sharper at higher fields. The shape of the ELT beyond the peak is then a direct measure of the diffusion profile. The appearance of the peak therefore marks the onset of the diffusive regime of carrier transport, whose validity is demonstrated next through simulations.

The transport of the charge packet into the layer would be subjected to drift and diffusion before recombination sets in. We go on to show through simulation that it is sufficient to consider these two basic processes to predict the shape of the EL transients observed. We do so using the ATLAS-Silvaco[25] platform and material parameters ($\mu_{0e} = 5\times10^{-8}$ cm^2 V^{-1} s^{-1} and $\mu_{0h} = 5\times10^{-6}$ cm^2 V^{-1} s^{-1}) adapted for organic devices. We do not assume a Gaussian distribution of states to suppress dispersive transport and only assume standard drift-diffusion equations. The normal Einstein relationship was used as a standard feature of the simulation platform. We monitor the recombination rate near the MEH-PPV/Ca interface in a trap-free case for different voltages noting that the recombination is directly proportional to the EL signal, with the lower concentration of the carriers being the rate-limiting species. Typical results of simulation for three different voltages are shown in Fig. 3. The profile so obtained is remarkably similar to the observed EL transients showing all the dominant features, such as peak movement due to the field, and change in shape (narrowing at higher field) due to diffusion from the leading edge.

To further ensure that diffusion indeed determines the transient shape, we deduce back D from the results of simulation. The inset of Fig. 3 shows the method of deriving D from the asymmetrical shape of the ELT. We analyze the tail beyond the peak to deduce D as per the standard

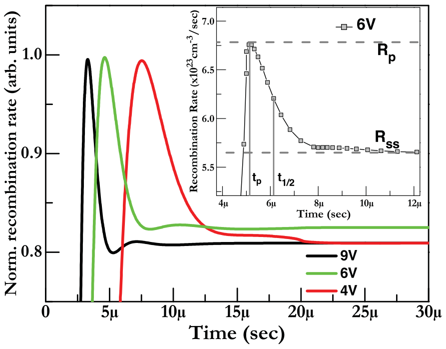

FIG. 3. (Color online) Simulated recombination rate (normalized) near the MEH-PPV/Ca interface at different voltage pulse heights. The inset shows peak and steady-state recombination rates R_p and R_{ss}, respectively, and t_p and $t_{1/2}$ used in determining D from Eq. (3). Note that standard band transport and Einstein relation is assumed, and there is no initial broadening at onset due to the absence of dispersion in the simulation.

Gaussian profile for the case of diffusion under constant total concentration of species.[23] It is straightforward to obtain D from the ratio of the height of the peak at t_p, and half of its value at $t_{1/2}$ on the tail side, which is the diffusive part of the transient.

The profile of charge carriers reaching the cathode, being proportional to the recombination rate, can be written as

$$n(d,t) = \frac{N_0}{\sqrt{4\pi Dt}} \exp\left(-\frac{(d-\mu Ft)^2}{4Dt}\right), \qquad (1)$$

where N_0 is the total number of diffusing species and d is the thickness.

The diffusion constant D can then be written in terms of t_p and $t_{1/2}$ as

$$D = \frac{1}{4\,\ln(2\sqrt{t_{1/2}/t_p})}\left(\frac{(d-\mu Ft_p)^2}{t_p} - \frac{(d-\mu Ft_{1/2})^2}{t_{1/2}}\right). \quad (2)$$

Assuming that the mobility is correctly obtained when the time of travel is t_p, (2) simplifies to

$$D = \frac{1}{2\,\ln(4t_{1/2}/t_p)}\left(\frac{d^2(t_p-t_{1/2})^2}{t_p^2 t_{1/2}}\right), \qquad (3)$$

a convenient expression depending on d, t_p, and $t_{1/2}$ only.

The value of D (along with its temperature and field dependence) obtained from such an analysis reproduces the input values, with χ varying between 0.9 and 1.67. Our simple analysis ignores the possible deviation of diffusion profile due to the influence of the field and its inhomogeneity, which can be argued to be insignificant for the present study. Hence, the simulations prove the validity of our assumption that the shape of EL peaks are diffusion limited, paving the way for determination of D from experimentally observed profiles.

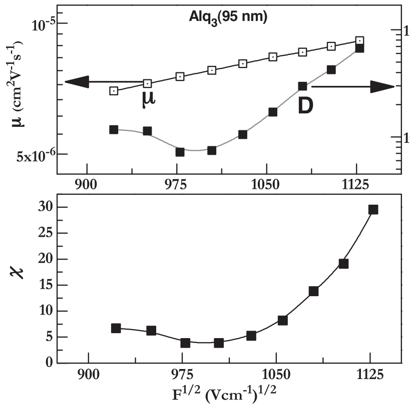

FIG. 4. Electric-field (F) dependence of diffusion constant D and mobility μ (upper panel), and Einstein coefficient χ (lower panel) for Alq_3 (95-nm-thick) shown as a function of $F^{1/2}$.

Having established the validity of the procedure, we return to our experimental results obtained from such an analysis, which are shown in Figs. 4 and 5 for Alq_3 and MEH-PPV, respectively. The parameters D and μ are obtained independently from the same experiments for both the materials. They are shown as a function of $F^{1/2}$, where F is the average field as in a traditional Poole-Frenkel (P-F) plot. The built-in potential for the two cases is experimentally measured reliably from the peak of capacitance-voltage characteristics for purposes of field correction. In Fig. 4, the upper panel shows the conventional P-F mobility (log μ vs $F^{1/2}$) plot which gives the P-F coefficient [defined as $\mu \sim \exp(\beta\sqrt{F})$] $\beta = 1.3 \times 10^{-3}$ (cm/V)$^{1/2}$ in agreement with reported values for Alq_3.[26] The directly determined D are also plotted along with μ in the same panel. To the best of our knowledge, there is no report of D for electrons in Alq_3 so far. The thermodynamic factor χ, as the ratio of measured D and μ values, is shown in the lower panel. Note that the χ is nonmonotonic with a decrease at lower fields dipping to nearly three for moderate fields and increasing further for higher fields, as in the case of Alq_3. This behavior cannot be understood merely by the concentration dependence of carriers which would monotonically increase with an increase in injection at higher fields.

Figure 5 shows the corresponding results for MEH-PPV with the Ca cathode. The mobility for the case of MEH-PPV with the Ca cathode shows negative P-F coefficient for low electric-field regimes, and we have recently discussed the

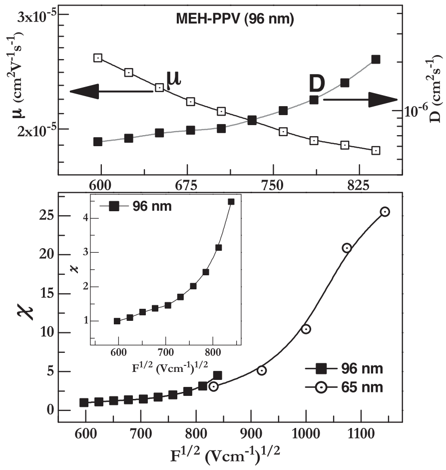

FIG. 5. Electric-field (F) dependence of diffusion constant D and mobility μ (upper panel), and Einstein coefficient χ (lower panel) for MEH-PPV shown as a function of $F^{1/2}$. The data in the lower panel are for two different thicknesses (65 and 96 nm) to cover a wide range of fields.

implications of this and attributed it to the injection of hot electrons and their transport through overlapping transport states of neighboring localized density of states (DOS).[18] However, the regime of field in which the peak appears in the MEH-PPV/Ca device, the effective mobility is dominated by hole mobility, as shown elsewhere.[18] At large electric fields copious electrons are injected but tunneling through transport states is difficult due to severe misalignment of localized DOS and electrons are forced to relax in the presence of localized states. The relaxation time is known to occur in a time scale much shorter than typical transit times in EL transient experiments.[27] Moreover, the larger the concentration of electron injected, the smaller the relaxation time since the capture time constant at traps is inversely proportional to the electron concentration. The electron concentration profile is thus large and sharp at the cathode as is ideal for our analysis. The lower panel of Fig. 5 shows the values of χ taken from measurements of two samples (96-nm- and 65-nm-thick films) to cover a wider range of effective field. The results for the thicker sample are shown in the inset for greater clarity. The only other reported values of D for MEH-PPV, using TOF as a technique, are unrealistically high, which is attributed to a combination of phenomena involving dispersion, traps, and disorder.[28]

The most significant feature of our results is that in a simple diode structure we are able to demonstrate D and χ as a function of electric field under normally employed transient conditions. In agreement with the traditional view, we consider that the broadened ELT onset is indeed due to dispersion of mobility (within the DOS) as the relaxation of carriers proceeds during transport. However, in the field regime in which peak is observed at the onset of ELT, we observe hardly any dispersion before the peak. This leads us to the conclusion that the carriers injected in this situation, behave like a packet of hot carriers. Being at higher energies they become insensitive to mobility dispersion, and diffuse in space away from the high-concentration leading edge. This is in tune with the original conjecture of Richert *et al.*[2] that at high energies, the carriers do not see most of the disorder, and rather find shortcut pathways to high-energy sites leading to diffusive motion in space. Therefore, it seems reasonable to consider that transport of sufficiently hot carriers can be adequately described by drift and diffusion alone. In our view, the diffusivity that we measure in the results presented here is that of hot carriers relevant to most transient applications in organic light-emitting diodes.

Our results on Alq_3 suggest an empirical linear relationship $\log D \mathrm{vs} F^{1/2}$ (Fig. 4) once the carriers are sufficiently hot in Alq_3; the onset of this regime possibly occurs at higher fields in MEH-PPV (Fig. 5). Hence, deviation from the Einstein relationship in such cases is more due to the system being in nonequilibrium rather than due to degeneracy of equilibrium statistics, as invoked by Tal *et al.* in the case of concentration dependence of mobility in thin film transistors.[16] In the case of ELT, the drifting carrier concentration does not have sufficient time to be in contact with localized states to make the quasi-Fermi level take position within the DOS. For Alq_3, the initial nonmonotonic variation with field is due to the partial opportunity of carriers to equilibrate within the DOS. In MEH-PPV, however, the electrons being injected high into the transport states equilibrate fast in contact with electron traps and provide a sharp profile at the cathode throughout the field regime in which the peak appears. The appearance of an EL onset peak at high electric fields is thus a convenient signature for the occurrence of nondispersive but diffusive transport of hot carriers.

In summary, we show that the simple experiment of electroluminescence transients is able to delineate field regimes for which the injected carrier concentration remains in nonequilibrium, wherein the diffusive component of jumps dominates over drift components increasing diffusion constant D and the thermodynamic factor χ. Such measured dependences for different materials can and need to be incorporated into the design of devices and simulation of operating conditions. A fit to the field dependence of D or χ would need better theoretical descriptions of hot carrier transport which our work is likely to stimulate for comparison with experimental results. In any case, the field dependence data can be directly used for purposes of simulation for better comparison with experimental data, a task currently underway in our laboratory.

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