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Effect of guest concentration on carrier transportation in blends of conjugated polymers

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In this paper, the charge transport in pure poly (9,9-dioctylfluorene-2, 7-diyl) (PFO) and its blend with poly (5-methoxy-2-2-ethyl-hexylthio)-p-phenylenevinylene (MEH-PPV) is studied. The mobility (μ_{eff}) and diffusivity (D) of the pure and blend thin films have been calculated using electroluminescence transient (ELT) technique. MEH-PPV concentration was varied from 0.8 to 15 wt%. It is found that at relatively low concentration of MEH-PPV, less than 1.2 wt%, the mobility of PFO:MEH-PPV blend increases with the concentration of MEH-PPV, and after that, it starts decreasing. The field dependence of effective hole mobility follows the Poole–Frenkel (P–F) plot of mobility (μ) as a function applied electric field with positive slope ($\beta_{PF} > 0$) up to 5.0 wt% concentration of MEH-PPV. A negative P-F type dependence is then observed for 8.0–15 wt% MEH-PPV concentration. Diffusivity (D) of blends is following the same trends as mobility *i.e.* blend with 1.2 wt% MEH-PPV shows the highest diffusivity. These results have been correlated with the morphology of pure and blend thin films. Gaussian Disorder Model (GDM) alone is not able to explain the change in β_{PF} with the MEH-PPV concentration, guest induced crystallization of PFO plays an important role at low concentrations of MEH-PPV. At higher concentrations of MEH-PPV ($\geq$8 wt%), crystallization is suppressed, and position disorder induced behavior of polymer determines the charge transport in the blends.

1. Introduction

The conjugated polymer blends have received significant attention in past few years because of their use in the polymer light emitting diodes (PLEDs) [1–5], organic thin film transistor (OTFT) [6–8] and organic photovoltaic (OPV) [9–11] devices. Polymer blending enhances electrical and optical properties of the host material. The carrier injection, carrier transport and electroluminescence spectra of the host polymer could be modified by a suitable choice of guest polymer, as well as by changing the concentration of a given guest polymer. Therefore, charge carrier transport characteristics of polymer blends have been the subject of many investigations.

The charge transport in organic/polymeric molecules is well described by a disorder hopping model having Gaussian distribution of hopping site energies and distances [12]. The rate of charge transport between the neighboring hopping sites will decide the charge carrier mobility in polymer systems. The empirical relation for the dependence of mobility (μ) on the electric field and a temperature is given by Gaussian Disorder Model (GDM) [12] as Eq. (1)

$$\ln \mu = \left[\ln \mu_0 - \left(\frac{4\sigma^2}{9k^2T^2}\right)\right] + \left[C_0\left(\frac{\sigma^2}{k^2T^2} - \Sigma^2\right)\right]\sqrt{E} \qquad (1)$$

Where μ_0 is zero field mobility, σ is the energetic disorder (the width of the Gaussian distribution of site energies), k is the Boltzmann constant, T is the temperature in Kelvin, C_o is an empirical constant, Σ is the measure of positional disorder, and E is corrected applied field.

The charge carrier hopping probability depends severely on the site energies and intersite distances. The positional disorder (Σ) comes from the morphological and spatial randomness of the dopant molecules dispersed in a host matrix. However, energetic disorder (σ) arises from the dipolar interactions between the guest molecules and with the host polymer molecules. It is evident from

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Eq. (1), that change in the position and energetic disorder with respect to applied electric field (E) and temperature (T) determines the positive or negative dependence of charge carrier mobility. A Poole- Frenkel (P-F) type mobility with a positive slope of $ln\mu$ versus $E^{1/2}$ curve have been observed in pure and blended conjugated polymer thin films [12]. The negative field dependence (NFD), *i.e*. a reduction in charge carrier mobility with an increase in the applied field, has also been reported in the literature [13–15]. It is explained on the basis of saturation of the charge carrier velocity (at high field) and large position disorder (at low field) [16].

The charge carrier mobility can also be changed by modifying the energy distribution and distance between the hopping sites. When we blend or dope a system, the dopant or guest molecule will additionally produce a random distribution of guest/dopant molecules in space and it will coulombically interact with the host at intrinsic hopping site and hence widen the effective density of state (DOS) distribution [17,18]. It also affects the mobility of charge carriers in the doped system. This also implies that changing the charge carrier density (by increasing electric field) in an energetically disordered hopping system will strongly modify the transport [19]. Conjugated polymer blends form an interesting platform to understand the effect of these disorders on carrier mobility. Further change in morphology due to phase separation adds another dimension to carrier transport studies in polymer blends.

In this article, we have studied the charge transport properties of PFO and PFO: MEH-PPV blends using electroluminescence transient (ELT) technique. PFO: MEH-PPV blend is a promising emissive layer for the development of white polymer light-emitting diodes [2,20–24]. In order to get the best performance from this material, there is a need to understand charge carrier behavior in the blend. With this as motivation, MEH-PPV concentration in PFO is being varied from 0.8 to 15 wt%. The carrier mobility and diffusivity, estimated from ELT, have been correlated with the observed morphology and structural characterization of pure and blend films. We report that the slope of the P-F plot (β_{PF}) also varies with MEH-PPV concentrations. We argue that GDM alone is not able to explain the electrical field dependence of mobility and β_{PF} on MEH-PPV concentration. Guest-induced crystallization plays an important role in determining charge carrier transport properties at low concentrations of MEH-PPV doping.

2. Experimental details

The conjugated polymers viz polyfluorene (PFO) and poly (5-methoxy-2-2-ethyl-hexylthio)-p-phenylenevinylene (MEH-PPV) were purchased from American Dye source and Sigma-Aldrich and used as received. The polymer light emitting diodes (PLEDs) were fabricated on indium tin oxide (ITO) coated glass substrates. Patterned ITO-coated glass substrates were cleaned by RCA solution followed by ultrasonication in deionized (DI) water, acetone, and isopropyl alcohol (IPA) sequentially and then dried in a vacuum oven. The cleaned and patterned ITO-coated glass substrates were subjected to ozone treatment for 20 min. After this, a hole injecting layer of poly-3,4-ethylenedioxythiophene-poly-styrenesulfonate (PEDOT:PSS) was spin coated on the ITO substrates and dried under vacuum for 1 h at the temperature 120 °C. The solution of pure PFO and PFO: MEH-PPV (0.8–15 wt%) blends were made in toluene/chloroform mixer and spin-coated on the top of PEDOT:PSS layer. Finally, the emissive layers were annealed at a vacuum of 5×10^{-6} mbar for 1 h at 140 °C. Calcium (Ca) and aluminum (Al) are thermally deposited as a cathode in high vacuum. The final device structure obtained was Glass/ITO/PEDOT: PSS/PFO: MEH-PPV (0–15 wt%)/Ca/Al. The PLED devices were encapsulated inside the nitrogen glove box to prevent from environmental degradation. The active area of the devices was 0.16 cm^2. The thickness of the active layer was measured using Alpha Step profilometer (KLA-Tencor). Surface morphology and phase analysis of the pure and blend thin films spin-coated on quartz substrate were carried out using Asylum research MFP-3D atomic force microscope (AFM) and grazing incidence X-ray diffraction technique (GIXRD) on a Panalytical MRD Pro X-ray diffractometer employing CuK_α radiation ($\lambda = 1.54056$ Å).

For ELT measurements, we have applied rectangular pulses using 50 Hz pulse generator (model no - HP 81101 A) having rise/decay time 10 ns with different magnitude of voltages and width (10 μs) across the PLED devices. Fig. 1(a) shows the schematic of the experimental set-up. The repetition rate of the pulse was kept 1 kHz to assure no disturbance of the subsequent pulses and ELT response as well. Also, function generator allows us to drive PLEDs with different offset voltage before applying the rectangular voltage pulses. The encapsulated devices were mounted on homemade PCB fixture with appropriate contacts of every device. An Acton Photo-Multiplier Tube (PMT S100) having time resolution <1 ns was placed on the top of the emitting side of the diodes to observe the EL emission from the samples. The entire setup is covered with black cloth to avoid any interference of the stray light in the room. The 500 MHz digital oscilloscope (HP 546153) with resolution 5 mV was connected through 50 Ω resistances to the PMT to capture the time-dependent EL signals. A personal computer was attached to the digital oscilloscope to collect experimental data. ELT technique is primarily based on monitoring time lag in EL due to applied voltage pulse. Fig. 1 (b) shows typical EL transients curve found in response to rectangular voltage pulse. The voltage dependent EL transient (ELT) signals of a PLED can be used to determine carrier mobility and diffusivity. All devices were characterized at room temperature and the applied electric field was $>4.2 \times 10^5$ V cm^{-1}. The analysis of these curves for each case will be discussed in the next section.

3. Results and discussion

3.1. Analysis of ELT curves

When we applied a rectangular voltage pulse across the device, holes are injected from PEDOT: PSS and electrons from calcium cathode, respectively. Under the external electric field, charge carriers move to opposite electrode to form excitons which emit light. The estimated time delay (t_d) between applied voltage pulse and an onset of EL signal will determine the effective mobility of carriers. However, in single layer PLED, the fastest carrier will determine the delay in EL signals as a result of applied voltage pulse. Therefore, in these experiments, we are measuring the effective mobility of holes in the pure PFO and its blends with MEH-PPV.

Fig. 2(a–g) shows ELT curves of PLEDs having pristine PFO and PFO: MEH-PPV blends as emissive layer. MEH-PPV concentration is varied from 0 to 15 wt%. ELT curves in each case are taken at different applied voltages at room temperature. The main characteristics of the ELT curves are the time delay (t_d) before EL onset, the appearance of an EL peak (at higher voltages), and steady state EL intensity at longer time duration. For lower voltages, the EL signal increases gradually saturate at a steady state value. At higher voltages, the EL signal increases sharply with the appearance of a peak in initial stages (switch-on peak) followed by decay of the signal to a steady state level in all the cases. The switch-on peak becomes narrower with further increase in the applied voltage. Since every part of the transient curve could provide information about carrier transport and recombination, the entire set of data is reported in Fig. 2.

A discrete peak in the EL transient signals at the switch-on edge [25–31] has been noticed by several researchers. Typically, the