Dipolar alignment and consequent enhanced charge transport in poly (9, 9′ di octyl fluorene)-2, 7-ylene ethylnylene

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Current density–voltage characteristics of poly (9, 9′ di octyl fluorene)-2,7-ylene ethylnylene thin films ($\sim$120 nm) have been studied in hole only device configuration at different temperatures (290–100 K) in unpolarized and polarized samples. The hole mobility has been found to be enhanced as a result of dipolar alignment by exposure to a dc electric field via cooling at all elevated temperatures. At higher field, current density has been found to be governed by trapped charge limited currents (TCLC) with hole mobility strongly dependent on electric field and their respective charge transport parameters have been obtained for both samples. The density of trap states has been found to be decreased on polarization from 1.1×10^{18} to 7.6×10^{17} cm^{-3} and trap energy has correspondingly decreased from 43 to 35 meV. The TCLC model with Poole–Frenkel-type field-dependent mobility has been fitted into the data and found to be in excellent agreement. Temperature dependence of zero field mobility (μ_0) and disorder parameter (σ) also has been estimated. We conclude that the relatively higher hole mobilities may be due to the orientational ordering of polar molecules and displacement of excess charges. © *2011 American Institute of Physics*. [doi:10.1063/1.3553845]

I. INTRODUCTION

Polymer electronics is one of the most interesting areas of organic electronics, especially for scientists and young researchers. The trend toward organic electronics raises a quiet interest toward the novel material to control the properties of the active material from macroscopic to microscopic scale. In contrast to inorganic semiconductors, organic semiconducting molecules, being small molecule or conjugated polymer, are inherently used in the area of organic electronics, viz:, organic light-emitting diode, organic photovoltaic and organic thin film transistors, etc. Conjugated polymers are the most promising candidate over the small molecules for technological application due to their good solubility, processability, and their environmental stability. Poly *p*-phenylenevinylene and its derivatives are the most significant materials for the fabrication of polymer light-emitting diodes and polymer photovoltaic devices due to their maximum absorbance and good photoluminescence in nature.[1–5] Presently, poly (9, 9′ dioctylfluorene) (PFO) is the most intensively investigated polymeric material for the light-emitting device applications due to very high hole mobility $\mu_h \approx 10^{-4}$–10^{-3} cm^2/V s, and in many cases these show non-dispersive hole transport at room temperature.[6–8] The performance of these devices depends primarily on the electrical conduction property of the polymers. However, to further improve the efficiency and stability of light-emitting diodes based on PFO, there is a need to understand device

physics in terms of charge carrier transport and innovate intrinsic/extrinsic ways to tailor/modulate[9,10] its charge transport parameters such as hole mobility, characteristic trap energy, density of hole traps, etc. Enhanced carrier mobility gives rise to improved device performance. Enormous efforts have been undertaken to enhance carrier mobility. It has been reported that the hole mobility of PFO thin films increases upon annealing in its amorphous phase, as well as its crystalline phase.[11,12] Homogeneous alignment of PFO films on rubbed polyimide also has been reported.[13] Keeping all in view, we have used a concept of polarization for the alignment of PFO thin films and studied its current–voltage J–V characteristics. In this polarization process, a fixed field (5×10^5 V/cm) was applied across the sample at an elevated temperature 290 K and subsequently cooled down to lower temperature up to 100 K in the presence of the applied field. The field was then removed and the sample was short-circuited for a few minutes to remove the stray charges present, if any. Then the J–V characteristics were studied at different temperatures in the range of 290–100 K.

In this paper we report the effect of polarization on the hole transport at various temperatures by performing the current density–voltage measurements. The hole mobility μ_h as a function of electric field (F) and temperature (T) of the form[14]

$$\mu(F, T) = \mu(0, T) \exp\left[\gamma(T)\sqrt{F}\right] \qquad (1)$$

has been obtained. This field and temperature dependence of hole mobility is called the Poole–Frenkel (PF) relation, where $\mu(0, T)$ and $\gamma(T)$ are the temperature-dependent

quantities, known as zero field mobility and field activation of the mobility, respectively. Generally, in most of the disordered organic molecular solids,[15,16] hopping among the molecular sites having comparable energies describe the transport of charge carriers through the Gaussian density of states of highest occupied molecular orbitals and/or lowest unoccupied molecular orbitals. Several disorder models for the charge transport have been debated to understand the role of spatial and energetic correlation in these systems. Such correlation has been compared to explain the universal electric field and temperature-dependent mobility [Eq. (1)]. Transport parameters (σ and Σ) extracted from field-dependence data have been found very close to the earlier reports.[12] A study of film morphology shows the clustering of molecules after polarization. Clustering of molecules provides an ordered path as compared to disordered system. This study affirms the significant role of polarization on the hole transport.

II. EXPERIMENTAL

Two different samples (designated as the unpolarized sample and polarized sample) were fabricated under identical conditions for unpolarized and polarized PFO (purchased from Aldrich chemicals) films in hole only device configurations, i.e., ITO ($\varphi \sim 4.8$ eV)/PEDOT:PSS (80 nm)/PFO ($\sim$120 nm)/Au ($\varphi \sim 5.2$ eV). Devices were grown on glass slides precoated with transparent ITO with sheet resistance of 18 $\Omega/\square$. Substrates were ultrasonically cleaned in detergent solution for about 10 min, followed by rinsing in deionized water. These are then boiled in acetone, trichloroethylene and propanol and dried in each step at 90 °C for 10 min. Thereafter a thin film (thickness $\sim$80 nm) of PEDOT:PSS (Aldrich USA) was spin coated onto the precleaned plasma-treated ITO coated glass substrates at 1500 rpm and cured at 120 °C for 30 min in vacuum. Further a homogeneous solution by dissolving PFO in chlorobenzene was prepared with material content of 10 mg/ml. Thin films of about 120 nm thickness were prepared by spin coating a chlorobenzene-based solution of PFO on precured PEDOT:PSS coated glass substrates in a nitrogen atmosphere of a glovebox. These films were then annealed at 150 °C in vacuum for 2 h (Ref. 17) and the film thicknesses were estimated by atomic force microscopy. On top of these films, Au electrodes of $\sim$500 nm thickness were deposited by vacuum thermal evaporation at 5×10^{-6} Torr. The devices so obtained were sealed using UV irradiated epoxy resin to inhibit atmospheric oxidation of electrodes. J–V characteristics of the unpolarized and polarized sample in different temperature range were measured using a low temperature setup coupled with a Keithley 2400 Source Meter unit interfaced with a PC. A scanning electron microscope is used to characterize the morphology of the sample.

III. RESULTS AND DISCUSSION

Figure 1 shows the J–V characteristics of configuration ITO/PEDOT: PSS (80 nm)/PFO (120 nm)/Au at room temperature. The experiment consists of two different samples, i.e., an unpolarized sample and polarized sample. It has been
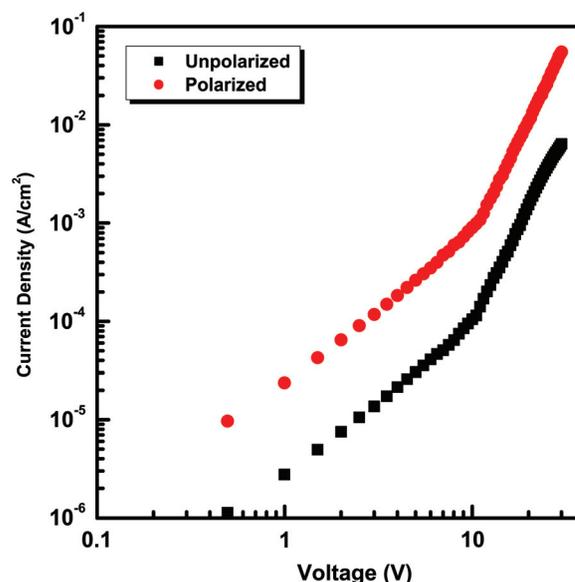

FIG. 1. (Color online) Room temperature J–V for single layer hole only PFO device with thickness of 120 nm: (a) unpolarized sample and (b) polarized sample.

found that there is considerable enhancement in current density in PFO thin films after polarization.

Figures 2(a) and 2(b) shows the temperature-dependent J–V characteristics of the unpolarized sample and polarized sample of the PFO polymer. The current density strongly depends on the applied bias and temperature. In several cases, the charge transport mechanisms have been well explained in noncrystalline organic semiconductors by space charge limited current (SCLC) and trapped charge limited current models (TCLC) and J–V behavior beyond Ohm's law follows:[18,19]

$$J = q^{1-l}\mu N_v \left(\frac{2l+1}{l+1}\right)^{l+1}\left(\frac{l}{l+1}\frac{\varepsilon\varepsilon_0}{H_b}\right)^l \frac{V^{l+1}}{d^{2l+1}}, \quad (2)$$

where J is the current density, V is the applied voltage, q is the elementary charge, d is the thickness of the material film, μ is the hole carrier mobility, and N_v is the effective density of states, H_b is the total trap density, ε is the dielectric constant of material, and ε_0 is permittivity of the free space. Where $l = 2$ in the case of SCLC and $l = T_c/T$ in the case of TCLC, T_c is the characteristic temperature of traps and d is the sample thickness. J–V characteristics follow square law ($J\alpha V^2$) at lower bias but as the bias increases, the slope of $l+1$ in the log–log plot of J vs V curve increases from $l = 2$.

To fit the experimental results, we have modified SCLC theory by solving the current density equation and Poisson's equation with electric field and temperature-dependent mobility of Eq. (1):[20–22]

$$J(x) = q\mu[F(x), T]p(x)F(x), \quad (3)$$

$$\frac{\varepsilon dF(x)}{edx} = P(x), \quad (4)$$

where $F(x)$ is the electric field, $p(x)$ is the hole density at position (x) and taking boundary conditions (i) electric field
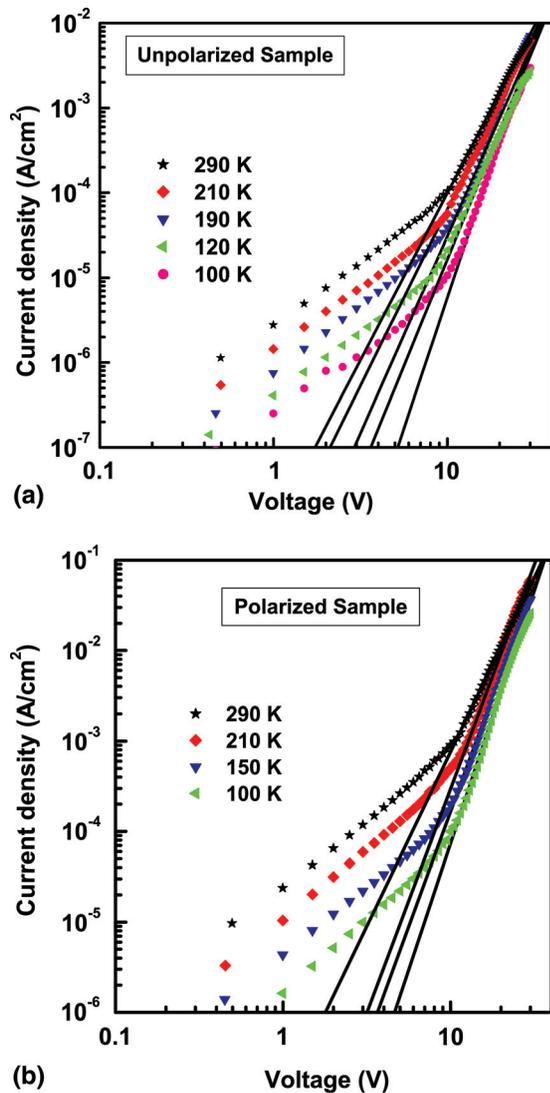
FIG. 2. (Color online) J–V characteristics of bulk limited current in ITO/ PEDOT:PSS/PFO/Au at different temperatures. Experimental data are shown by symbols and solid lines represent the theoretical fits for (a) unpolarized sample and (b) polarized sample.

FIG. 3. (Color online) Temperature dependence of *l* obtained from theoretical fit according to the TCLC law to the experimental data (shown in Fig. 1) for the unpolarized sample and polarized sample.

vanishes at $x = 0$ (ii) hole density is equivalent to the density of states ($N_v = 1 \times 10^{19}$ cm^{-3} at $x = 0$).

The theoretically generated curves from Eqs. (2) to (4) in Figs. 3(a) and 3(b) give a perfect fit to the experimental curves for all analyzed temperatures with fitting parameters $N_v = 2.7 \times 10^{18}$ cm^{-3}, $H_b = 1.1 \times 10^{18}$ cm^{-3}, $\mu = 3.5 \times 10^{-5}$ cm^2 V^{-1} s^{-1}, and $T_c = 500$ K for the unpolarized sample and $N_v = 2.7 \times 10^{18}$ cm^{-3}, $H_b = 7.6 \times 10^{17}$ cm^{-3}, $\mu = 7.6 \times 10^{-4}$ cm^2 V^{-1} s^{-1}, and $T_c = 406$ K for the polarized sample. The theoretical curves follow $J \alpha V^l$ dependence where $l = 2$ at lower fields and increases gradually with higher fields. In the TCLC model the value of exponent l is given by T_c/T, where T_c is the critical temperature (characteristic trap energy E_t is given by: $E_t = kT_c$) and is a constant. We obtained the l values in this trap-filling SCLC regime and plotted them as a function of the inverse of the temperature in Fig. 3. The value of trap energy has been calculated from this plot. The characteristic trap energy reduces from 43 to 35 meV on polarization.
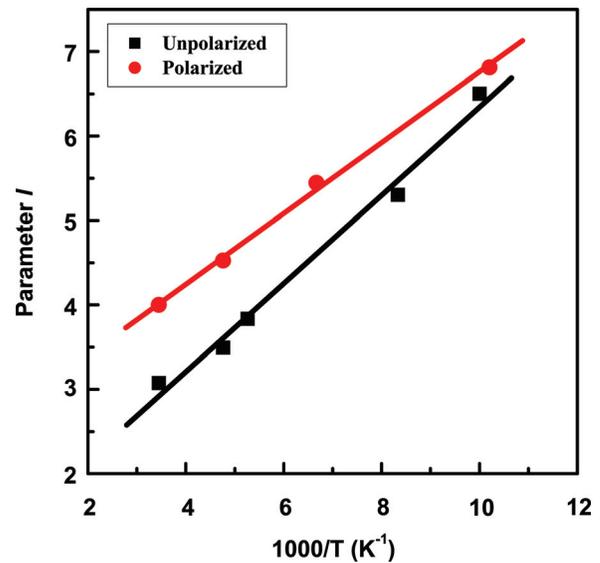
The TCLC model is developed for field-independent charge carrier mobility. However, the mobility in organic semiconductors is dependent on electric field. Therefore we have included a field-dependent mobility of the PF type $\mu(F, T) = \mu_0 \exp[\beta(T)\sqrt{F}]$ with parameters μ_0 and β to be determined for each temperature, where μ_0 is zero field mobility and $\beta(T)$ is the field activation energy and comparable to Poole–Frenkel-type coefficient. The analysis has been performed on both samples. Variation of μ_0 and β with $1000/T$ has been estimated from the TCLC model with Poole–Frenkel-type mobility for hole only devices with (a) unpolarized sample and (b) polarized sample of PFO. Values of μ_0 and $\beta(T)$ have been varied to fit the experimental data. The fitted values of μ_0 and β for both samples have been plotted with $1000/T$ in Fig. 4. From Fig. 4 it can be seen that the zero field mobilities μ_0 for both samples are 1.82×10^{-4} and 3.3×10^{-3} cm^2/V s, respectively, at room temperature. This shows that the mobility increases on polarization. Zero field carrier mobility μ_0 has been found highly temperature dependent, which is expected for disordered materials. The value of β increases with the decrease in temperature. This means that the field dependency of mobility increases with the decrease in temperature, which is observed by many authors.[23]

In disordered materials, charge transport generally takes place by hopping in a manifold of localized states, according to the Gaussian disorder model (GDM).[24] The latter is considered to be a Gaussian characterized by its standard deviation σ, which reflects the width of the transport manifold and is also known as the energetic disorder parameter. Accordingly, the temperature dependence of the zero field mobility is given by

$$\mu(0, T) = \mu_0 \exp\left[-\left(\frac{2\sigma}{3k_B T}\right)^2\right], \tag{5}$$

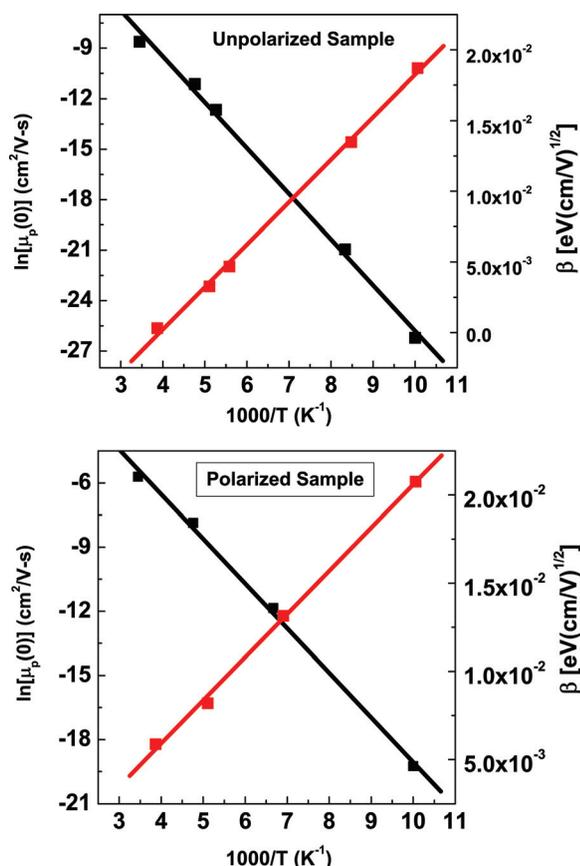FIG. 4. (Color online) Temperature dependence of zero field mobility (μ_0) and β estimated from theTCLC model with Poole–Frenkel-type mobility for hole only devices for the (a) unpolarized sample and (b) polarized sample.

FIG. 5. (Color online) Temperature dependence of zero field mobility (μ_0) according to GDM for hole only devices for both samples, i.e., unpolarized sample and polarized sample.

where μ_0 is the high temperature limit of the zero field mobility, k is the Boltzmann constant, and T is the absolute temperature. Variation of zero field mobility (μ_0) and σ with $(1000/T)^2$ has been estimated from the TCLC model with Poole–Frenkel-type mobility for hole only devices with (a) an unpolarized sample and (b) the polarized sample of PFO. Values of μ_0 and σ have been varied to fit the experimental data. The fitted values of μ_0 and σ for both samples have been plotted with $1000/T^2$ in Fig. 5. From Fig. 5, it can be seen that the energetic disorder gets decreased from 57 to 50 meV, respectively, at 300 K.

In addition to energetic disorder, there is disorder in the position of the hopping sites, characterized by the positional disorder parameter $\sum$. The latter $\sum$ was extracted from the plot of β vs $(\sigma/kT)^2$ (not shown) and was found to be increased from 1.9 to 3.11 on polarization. These results show that polarization of polymers by exposure to a dc electric field via cooling is indeed a very promising route to achieve high mobility in hole transporting polymers.

Further, the mechanism responsible for the positive change in transport parameters and current density on polarization has been explained in this view. Clustering and nanocrystallization of PFO has been observed after exposing the film to a dc electric field. These nanocrystallites in the polarized sample give the low value of energetic and positional disorder as compared to the unpolarized sample. When the
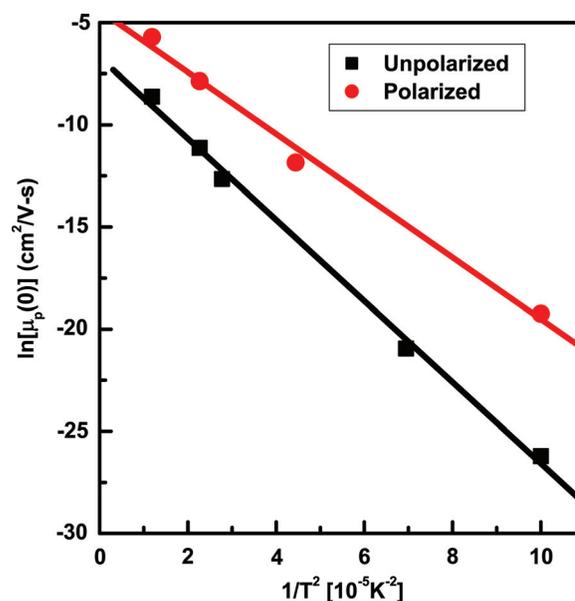
sample is polarized by applying a fixed electric field at an elevated temperature and cooled down to lower temperatures in the presence of the applied field, it generates internal polarization electric field in the frozen state of the sample. In this case, the net positive change in charge transport parameters of the polymer can be understood either as the orientational ordering of polar molecules and further displacement of excess charges or in terms of alignment of dipoles of PFO in the direction of the field and their subsequent freezing. (I) Application of a static electric field during polarization was found to inhibit (but not eliminate) the formation of cluster as seen in the scanning electron microscope (SEM) image in Fig. 6. It is clearly seen from the SEM micrograph that
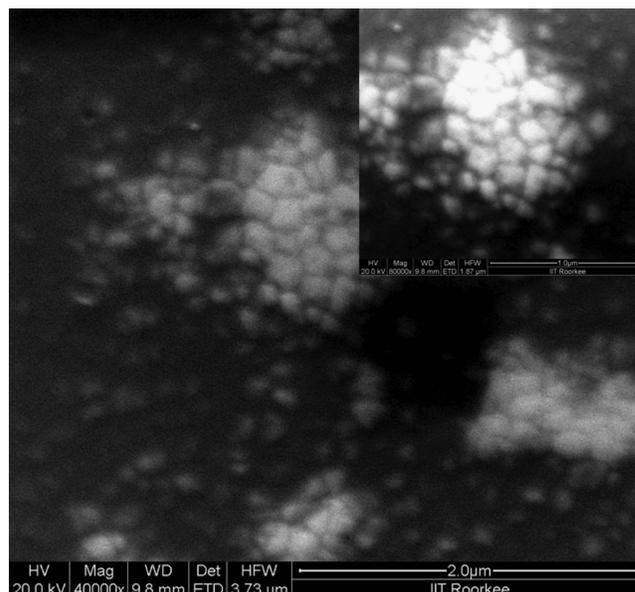

FIG. 6. SEM micrograph of charged thin film of PFO (inset shows magnified view).

indeed an increased order is established at these grain boundaries on polarization. Grain boundaries may lie parallel to the direction of current flow, which facilitates the holes transport and thus increases the carrier mobility. Grain boundaries act as surface states for charge carriers and can be accumulated. During polarization; the charges generated during the discharge are trapped in these surface states. This may result in the net decrease of characteristic trap energy and density of traps. Due to these reasons, the charge carriers become highly mobile due to enhanced order and in turn the enhancement in current density has been observed in this investigation.

(II) At the interface between organic materials and substrates, e.g., metal, excess electrons or holes are displaced from metals into organic materials. As a result, surface potential is built across organic materials deposited on substrate. This surface potential is considered as the sum of the surface potential due to excess charges, alignment of constituent dipolar molecules of organic materials and also surface charge, which is coming from another origin such as an absorbed molecule entering into the nanocrystalline sites of the polymer. These are supposed to promote the trapping of charge carriers. In organic semiconductors, electron transfer from metal to films is restricted within the region of several nanometers from the metal semiconductor interface. Further, the electron-transfer occurs so that the alignment of surface Fermi-level is established at the metal surface. In particular, the excess charges displaced from metal electrodes are immobile ones such as trapped electrons; the formed space charge barrier prevents further charge injection in a manner similar to that seen as space charge limited current. However, when the sample is polarized by applying a fixed electric field at an elevated temperature and cooled down to lower temperatures in the presence of the applied field, the nanodomains would then feel a torque given by $p \times E$ (E is the applied external electrical field) and this torque of external electric field facilitates excess electron motion from the metal surface becoming mobile just like electron gas. Thereby, conductivity of organic materials, i.e., mobility, increases.

IV. CONCLUSION

It is established that polarization plays a significant role in controlling the hole transport in PFO thin films. The charge transport, in both cases, is well explained by TCLC model with field dependent mobility. On polarization the transport parameters H_b, T_c, and E_t reduce from their respective values from 1.1×10^{18} to 7.6×10^{17} cm^{-3}, from 500 to 406 K, and from 43 to 35 meV. In addition, μ increases from 3.5×10^{-5} to 7.6×10^{-4} cm^2 V^{-1} s^{-1}. It all in turn results in enhancement in the current density in polarized PFO films. We also have shown that the charge carrier conducts through hopping, which is described with the Gaussian disorder model, signifying the important role of both energetic and positional disorder on the carrier transport in given J–V characteristics of hole only devices. These effects have been attributed to enhanced order due to displacement of charge carriers at microscopic distances and their subsequent trapping at grain boundaries or orientational ordering of polar molecules and further displacement of excess charges at the interface.

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