Giant anisotropy of carrier mobility in electroluminescent conjugated polymer

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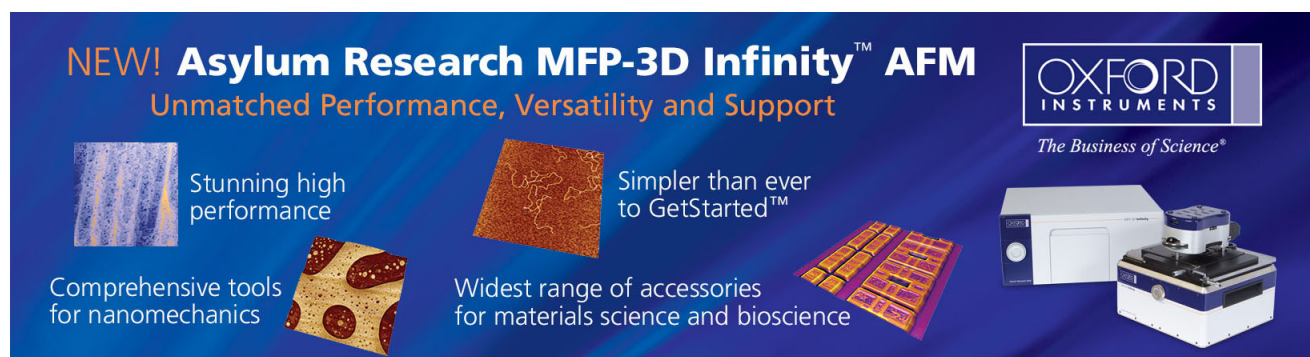Measurements of charge mobility and diffusion coefficient of conjugated electroluminescent polymers by time-of-flight method
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Giant anisotropy of carrier mobility in electroluminescent conjugated polymer

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The horizontal and vertical hole mobility of amorphous spin-coated electroluminescent conjugated films are studied. It is found that the horizontal mobility is about four orders of magnitude larger than the vertical mobility. The horizontal mobility increases daily with the aging of the polymer solution from which the film is spun. Low temperature and photoluminescence study reveal that the giant mobility anisotropy is a result of the alignment of the aggregates, formed during aging, by the centrifugal force of the spin. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2158517]

In most of the conjugated polymers device structures a thin polymer film is formed by spin coating. The polymer chains are amorphous in such films. The carrier motion in the typical sandwich light-emitting diode structure is vertical to the film, with mobility as low as 10^{-10} m^2/V s.[1,2] The model for vertical carrier transport has been established.[3] Surprisingly, there are very few studies on the carrier transport horizontal to spin-coated amorphous conjugated polymer films, which is of equal fundamental importance.[4] Because of the horizontal centrifugal force during the spin, the morphology of the resulting film can hardly be isotropic. In fact, optical measurement revealed that the polymer chains are mostly aligned along the substrate.[5,6] In addition, the relation between morphology and mobility anisotropy and the way to control the mobility are by themselves outstanding open questions. In this work we found that the horizontal mobility is indeed larger than the vertical mobility for as much as four orders of magnitude; 10^{-6} m^2/V s is reached at the field of 5×10^7 V/m. This is the largest mobility ever reported for amorphous polymer films. Such value is close to the mobility of self-assembled ordered structure of nonemissive polymers.[7] We discovered that the ultimate horizontal mobility in the film is actually determined by the evolution of the chain morphology in the parent solution which leads to aggregates. Spin coating transfers such aggregates into the film. The centrifugal force is shown to be required to align the aggregates into the large hopping domains, which consequently cause the giant anisotropy.

We obtain the hole mobility by fitting the space-charge-limited current (SCLC). The SCLC current-voltage relation is[8] $J=(9/8)\epsilon\mu(E)V^2/L^3$. J is the current density. L is the distance between the electrodes. V is the applied voltage. $E=V/L$ is the average electric field, μ is the mobility, ϵ is $\epsilon_0\kappa$, where ϵ_0 is the vacuum permittivity and κ the dimensionless dielectric constant. By fitting the experimentally measured J–V relation with the expression above one obtains the field-dependent mobility $\mu(E)$. The SCLC method can be applied for both vertical mobility μ_v and horizontal mobility μ_h; μ_h can also be measured by the characteristics of field-effect transistors (FETs). The saturation drain current I_d is given by[9] $I_d=W\mu_h C_{\text{ox}}(V_g-V_t)^2/2L$, where W is the channel width and L the channel length. C_{ox} is the capacitance of the gate insulator. V_g is the gate voltage and V_t the threshold voltage. At saturation the drain voltage V_{ds} is V_g-V_t, so the average electric field E in the channel is V_{ds}/L. From I_d–V_g relation at saturation we obtain the field-dependent horizontal mobility $\mu_h(E)$.

In addition to E, the mobility may also depend on the carrier density n if n is close to the degenerate regime. For a consistent study of mobility anisotropy, one needs to estimate n and make sure that we are far away from degeneracy for both vertical and horizontal transport. Consider the typical electroluminescent conjugated polymers poly (2-methoxy-5 (2′-ethyl-hexyloxy) -1,4-phenylene vinylene) (MEH-PPV) where the chains are packed in the locally ordered structure[10] with cell volume for each monomer equal to 15 Å $\times$ 3.56 Å $\times$ 6.65 Å $=335$ Å.[3] The monomer density n_0 is 1/355 Å$^{-3}=2.8 \times 10^{21}$ cm^{-3}, which is the effective density of states. In SCLC the carrier density $n(x)$ is $(1/e)\sqrt{\epsilon J/2\mu x}$, where x is the distance from the injection electrode.[8] Averaging $n(x)$ from $x=0$ to $x=L$, the mean carrier density n is given by $n=(2/3)\epsilon E/eL$. The dielectric constants are $\kappa_h=3$ in horizontal direction and $\kappa_v=2.4$ for vertical direction.[6] For vertical transport we take $L=0.1$ μm and maximal field $E=8 \times 10^7$ V/m. The resulting n_v is 7.2×10^{16} cm^{-3}. For horizontal transport we take $L=3$ μm and maximal field $E=8 \times 10^7$ V/m. The resulting n_h is 3×10^{15} cm^{-3}. Both n_v and n_h are 5–6 orders of magnitude smaller than n_0, so the SCLC transport is safely in the nondegenerate regime and the carrier mobility should not depend significantly on the carrier density. On the other hand, for FET the nondegenerate condition does not hold so well. In FET the surface charge density σ of the accumulation layer is related to the gate voltage by[9] $\sigma/C_{\text{ox}}=V_g$, where $C_{\text{ox}}=\epsilon_{\text{ox}}/d$; d is the insulator thickness. The vertical surface electric field E_s is given by $E_s=(\epsilon_{\text{ox}}/\epsilon_0\kappa_v) E_{\text{ox}}=(C_{\text{ox}}/\epsilon_0\kappa_v) V_g$. The range of vertical distribution l of the holes in the accumulation layer is roughly $l=k_B T/(eE_s)$, where k_B is the Boltzmann constant and T is the temperature. The FET hole density n_f is therefore $n_f=V_g^2\kappa_{\text{ox}}^2\epsilon_0/(k_B T\kappa_v d^2)$. For SiO$_2$ $k_{\text{ox}}=3.9$; d is taken as the

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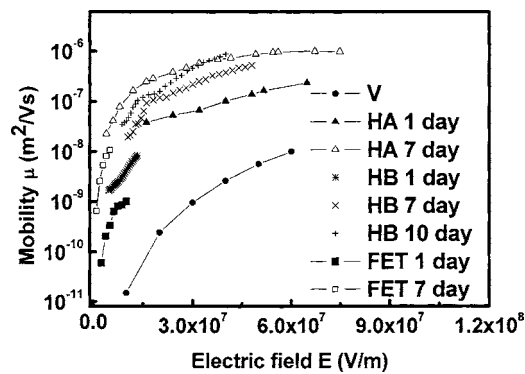
FIG. 1. The vertical mobility μ_v (V) and horizontal mobility μ_h (HA,HB, FET) of MEH-PPV are shown as functions of averaged electric field E. The number of days indicates the time of solution aging at room temperature (20 °C). Data HA and HB are obtained by SCLC fitting. The channel length L is 3 μm for HA and 2.5 μm for HB. μ_v does not depend on aging; μ_h increases with the aging time. In general, μ_h is much larger than μ_v.

FIG. 2. The mobilities at various temperatures are plotted against the square root of the field. They follow the form $\mu = \mu^* e^{-\Delta \beta} e^{\gamma \sqrt{E}}$; μ_h and μ_v share roughly the same slope $\gamma \simeq 1.5 \times 10^{-3} \sqrt{m/V}$. $\Delta \simeq 0.15$ eV, obtained from the slope in the inset, is also independent of the transport direction. The prefactor μ^* differs by several orders of magnitude.

maximal value 3000 Å. The resulting FET hole density n_f is 2.6×10^{20} cm^{-3} at $V_g = 40$ V. Such n_f is only one order of magnitude smaller then n_0. In other words, we are in the degenerate regime where the mobility possibly depends on the carrier density.[10] Due to such a high carrier density FET is not used as the main method for our experiments below. The very low carrier density for SCLC, on the other hand, implies that any difference between μ_v and μ_h can only result from the morphological anisotropy in the polymer films, i.e., it represents the "real" anisotropy.

For vertical transport we fabricate device with MEH-PPV sandwiched between indium tin oxide (ITO) anode and Al cathode. A layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulphonic acid) is placed between ITO and MEH-PPV for better hole injection. MEH-PPV with molecular weight 10^6 is synthesized; 1000 Å polymer film is spin coated. For horizontal transport we fabricate horizontal Au electrodes, similar to the source and drain of FET, on a glass substrate. The channel length L varies from 2 to 3 μm. We also fabricate FET structure for comparison. Indium tin oxide (ITO) is used as the gate, SiO$_2$ of 3000 Å as the insulator, and Au as source and drain (2000 Å). The channel length L is 5 μm.

In Fig. 1 we show the vertical mobility μ_v and the horizontal mobility μ_h of MEH-PPV, obtained from SCLC depends on many process conditions to be discussed below, while μ_v is basically independent of the process. Let us focus first on the optimal condition (open triangle) which gives the largest μ_h; μ_v is between 10^{-11} m^2 and 10^{-8} m^2 V s, similar to the values reported before.[2] The striking feature is that μ_h is 3–4 orders of magnitude larger than μ_v. Despite being amorphous, μ_h reaches as high as 10^{-6} m^2/V s at field around 5×10^7 V/m. Because the carrier density in the horizontal SCLC is even smaller than the vertical SCLC, the much higher horizontal mobility cannot come from the difference in carrier density as proposed earlier.[11] Interestingly, the highest FET mobility (open square in Fig. 1) is close to the SCLC mobility (open triangle). This implies μ_h does not depend on the carrier density n significantly even for n around 10^{20} cm^{-3}. The only possibility for $\mu_h \gg \mu_v$ is therefore the intrinsic anisotropy in the morphology of the polymer chains.

In order to understand the origin of the anisotropy, we measure the mobility at different temperatures. Figure 2
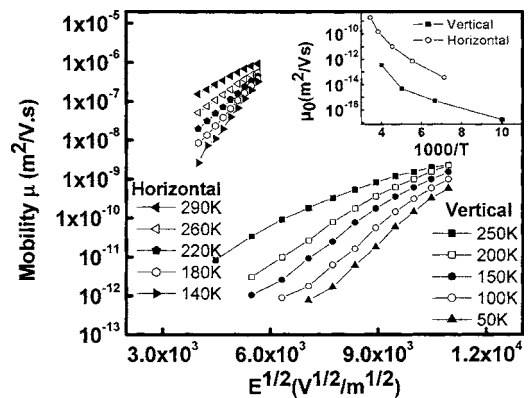
shows the temperature dependence of μ_h and μ_v. Both mobilities follow the Poole–Frenkel form $\mu = \mu^* e^{-\Delta \beta} e^{\gamma \sqrt{E}}$, which is typical for hopping transport. $\beta = 1/k_B T$; γ is similar for μ_h and μ_v as seen in the slopes of the plots. The energy barrier Δ for hopping is obtained by plotting the extrapolated zero-field mobility μ_0 vs $1/T$. The slope is also similar for μ_h and μ_v as shown in the inset; γ lies between 10^{-3} and $2 \times 10^{-3} \sqrt{m/V}$ depending on the temperature, Δ is about 0.15 eV. The only major difference between horizontal and vertical transport is μ^*, which accounts for the 10^4 difference in the mobility. Both Δ and γ reflect the energy barrier for hopping between sites. For vertical transport the sites correspond to conjugation segments with various conjugation length and therefore various on-site energies.[4] Δ is roughly the variance of the energy distribution. Similar γ and Δ imply the energy disorder among hopping sites in the horizontal direction is of the same origin. On the other hand, μ^* reflects the real-space distance for each hopping. The much larger horizontal μ^* suggests that the effective hopping site is much larger than just one conjugation segment. Somehow the segments arrange in such a morphology that ordered domains, i.e., the "sites," are formed horizontally and the holes move easily inside the domains and hop across the energy barriers only when they reach the boundary of the domains. We suspect that the domains consist of polymer chain aggregates, which form locally crystalline regions.[10]

For MEH-PPV film spun from chloroform solution μ_h is found to increase with the concentration. This is the first sign that aggregate is critical to the mobility. Based on 0.38 wt% chloroform solution, many process conditions are tested to control the mobility. Surprisingly, the single most important condition for μ_h is not anything that one does to the film itself, e.g. baking and annealing. Instead it is the "aging" of the parent solution that matters most. By aging we mean the time interval between the dissolution of MEH-PPV and the spin. In Fig. 1 we show how the mobility depends on the aging time at room temperature (20 °C). The mobility increases daily and saturates only after as long as ten days. This is true for both SCLC (data A and B) and FET. The formation of aggregates or whatever morphology features responsible for the giant anisotropy must have already taken place in the solution. PL spectra for various aging time confirm this picture. There are two peaks in the photolumines-
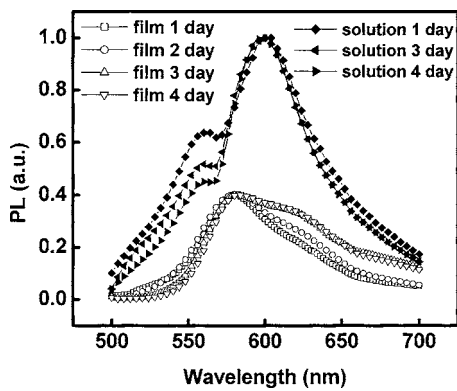
FIG. 3. The normalized PL spectra of solution after different aging time at 20 °C are shown. The aggregate peak at 620 nm grows relative to the isolated chain peak at 580 nm slowly with time. The growing 620 nm peak is transferred to the film formed by spin coating. The maxima of film PL are normalized to 0.4 for clarity.

FIG. 5. The film PL spectra demonstrate aggregates are destroyed by the high spin speed. Maximum horizontal mobility is reached at the optimal spin speed of 2000 rpm. SCLC and FET are the measurement methods. The FET results and SCLC results for 2000 rpm are connected by a dash-dotted line as a guide for the eyes.

cence (PL); 580 nm is due to isolated chain while 620 nm is due to aggregates.[12] The relative intensity of the 620 nm peak grows by days in solution (Fig. 3), meaning the aggregates form gradually during aging. This feature is transferred to the film PL, with overall suppression of 620 nm peak by the spin. This is a clear indication that, far from being static, the solution undergoes a constant evolution in its microscopic morphology. We also discovered that the slow aggregate formation can be made much faster by slightly increasing the aging temperature to 40 °C. At 40 °C the aggregate formation reaches saturation in two days, about five times faster than 20 °C. We show in Fig. 4 the solution PL after two-day aging with various aging temperatures. At high temperature (40 °C) the 580 nm peak for isolated chain becomes almost invisible. On the other hand, at low temperature (5 °C) the spectra is almost the same as just dissolved. The solution PL feature is translated to film as shown in Fig. 4. At low temperature the chain motion is frozen and the aging has virtually no effect. The inset of Fig. 4 shows that the mobility is lower for low-temperature aging. This is expected because the high μ_h requires a large amount of aggregates. Finally, we found that μ_h also depends on the spin speed significantly. In Fig. 5 we show film PL with different speed. The 620 nm shoulder is the highest in the drop cast film (zero spin speed) and decreases with the spin speed. Apparently

the centrifugal force tends to destroy the aggregate as reported before.[12] One would expect that the drop cast film, with most aggregates, gives the maximal μ_h. The answer is the opposite as shown in Fig. 5. Drop cast film has the lowest mobility, while 2000 rpm gives the highest. This proves that the mobility is determined by two competing factors. Aggregates are needed in the first place to form the large hopping domains. High spin speed destroys the aggregates and could lower the mobility. Nevertheless, the centrifugal force of the spin is required after all to align the aggregates in some anisotropic manner. Despite having the highest amount of aggregates, the drop cast film lacks the alignment so its μ_h is the lowest. In fact, it is close to μ_v, further indicating the isotropic morphology without the spin.

In conclusion, we show that there is a giant mobility anisotropy in polymer film resulting from the slow aggregate formation in the parent solution. Our work opens the possibility of field-effect transistor based on electroluminescent amorphous polymers with morphology control.
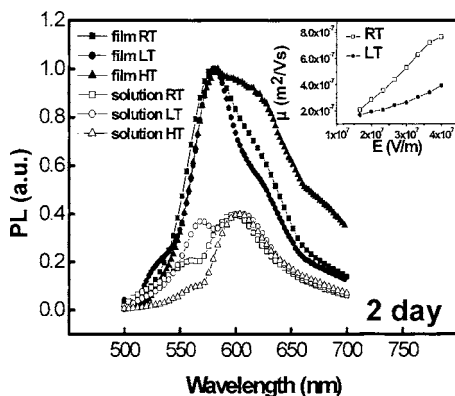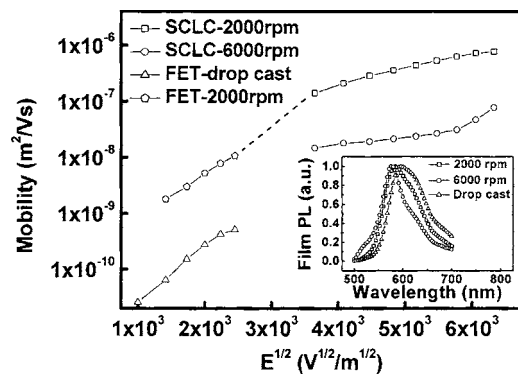
FIG. 4. The solution and film PL spectra at fixed two days of aging with various aging temperatures are shown. LT is 5 °C, RT is 20 °C, and HT is 40 °C. There are more aggregates as the temperature increases. Accordingly, horizontal mobility also increases with aging temperature as shown in inset.

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