Electron transport and electroluminescent efficiency of conjugated polymers

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ABSTRACT

The relation between charge balance and electroluminescent efficiency for polymers is studied systematically in this work. Light-emitting diodes of several kinds of polymers with very different efficiency are compared. The electron and hole currents are measured in the uni-polar devices and fitted by the theoretical model to get carrier mobilities. The universal features of the high efficiency polymers are that the electron and hole mobilities are comparable and the electron current is larger than the hole current due to the higher hole barriers. The electron current is more crucial than hole current to determine the efficiency in the bipolar light-emitting diode. The purity of polymers and low electron injection barriers both play significant roles in producing stronger electron currents. These results give the physical rules for designing new polymers and the device structures to achieve highly electroluminescent devices.

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1. Introduction

Polymer light-emitting diodes (PLED) attract a great deal of attention due to its easy process, high efficiency, and many new optoelectronic applications [1]. There have been a constant progress in improving PLED efficiency from molecular and device structure designs [2–4] Device models have been established and successfully explained many experiment results [5,6] In general, there are two factors that determine the electroluminescence (EL) efficiency, including electron–hole charge balance in the diode and thin-film photoluminescence (PL) quantum efficiency of the luminescent materials. For PL quantum efficiency the most commonly used polymers based on polyfluorene (PF) and poly(p-phenylene-vinylene) (PPV) all have very high PL quantum efficiency ranging from 15% to 50%. However, not all the materials with high PL efficiency will simultaneously yield high EL efficiency, indicating that the obstruction to high EL efficiency is charge balance. There are two elements which determine the individual charge currents. One is the carrier injection barrier and the other the carrier mobility. Much effort has been devoted to improving carrier injection, including electrode modification and adding hole (electron) injection layers [7,8]. For carrier mobility, the most unique and commonly known property of conjugated polymer is that the hole mobility is often much higher than the electron mobility [9,10] Yet so far, there is no direct report focusing on the relation between carrier mobili-

ties and EL efficiency. In this paper, we systematically study and compare the charge balance of several PF and PPV based polymers which all have high PL quantum efficiency. We find that high EL efficiency polymers have two distinguishing features: one is comparable electron and hole mobilities, and the other is that electron current is even larger than hole current under uni-polar injection. This result confirms that many polymers have high PL efficiency but poor EL efficiency due to the low electron mobility and imbalanced currents between electron and hole. The huge difference in electron mobility among the polymers is attributed to extrinsic effects like impurity and molecular weight which causes electron traps but do not quench excitons and reduce PL. This paper is organized as follows: Section 2 discusses the devices preparation and device model. In Section 3 we discuss the results. Section 4 draws the conclusion.

2. Device structures and theoretical models

In this work, three kinds of devices are studied, including hole-only device, electron-only device and bipolar device. Hole-only and bipolar device structures are ITO/PEDOT:PSS/polymer/Al and ITO/PEDOT:PSS/polymer/LiF/Ca/Al, respectively. ITO is indium tin oxide and PEDOT:PSS is poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate). Electron-only device structure is Al/polymer/LiF/Ca/Al. Fig. 1 shows the schematic electronic energy profile for electron-only and hole-only devices. Polymers are dissolved in organic solvent like xylene or toluene and then spin coated to make a 100 nm thin film followed by a baking process in vacuum (10^{-3} Torr) at 120 °C. The anode and cathode metals are evaporated by an evaporator in a glove box in high vacuum

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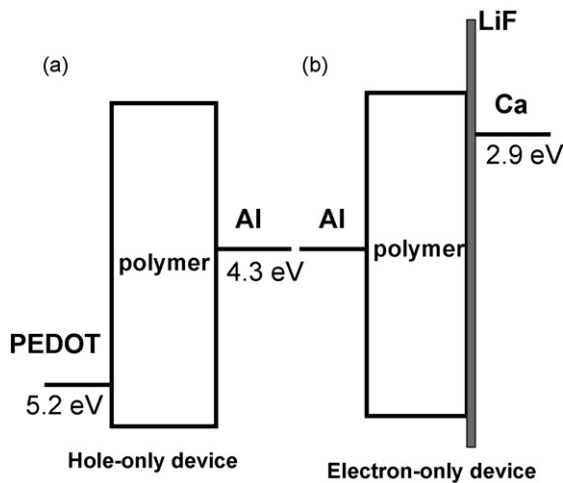
Fig. 1. Schematic electronic energy profile for uni-polar devices. (a) Hole-only and (b) electron-only devices. Work functions of the electrode are indicated.

(<10^{-6} Torr). Finally, all the devices are packaged in the glove box. In this paper six polymers are chosen to study the properties of transport and EL efficiency. Two high efficiency polymers, LUMATION BP105 (from the Dow Chemical Company) [14] and Super-Yellow (from the Covion Organic Semicondutors now Merck) [15] and the other four less efficient polymers, including poly (9,9-dioctylfluorene) (PFO, purchased from American Dye Source (ADS)), poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl))diphenylamine)](TFB, purchased from ADS), poly[(2-(4-(3,7-dimethyloctoxy)phenyl)-3-phenyl-1,4-phenylene-vinylene) (DPOC10PPV, synthesized in our lab) and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV, purchased from ADS) are studied in this paper. The electron affinity (EA), ionization potential (IP), PL efficiency and PL wavelength of polymers are shown in Table 1. We use 3.0 eV for EA of PFO from the optical band gap, such value is larger than the value of 2.1 eV obtained from cyclic voltammetry. [11] 3.0 eV is however more reasonable since PFO has an Ohmic contact with low work function metals. [12] The current–voltage relations are measured by HP 4157 semiconductor parameter analyzer. The film thicknesses are measured by Kosaka ET4000 Surface Profiler. The EL efficiencies are measured by Photo Research PR650 spectrophotometer integrated with Keithley 2400 multimeter. The PL efficiency is measured by an integrating sphere system.

The device models are reported elsewhere. [5,6,16] The charge transport with field-dependent mobilities and Langevin bimolecular recombination are described by the following equations:

$$J_e(x) = e\mu(x, E)\left[n(x)E(x) + \frac{kT}{e}\frac{dn(x)}{dx}\right] \quad (1)$$

$$\frac{dE(x)}{dx} = \frac{e}{\varepsilon}[p(x) - n(x)] \quad (2)$$

$$\frac{dn(x)}{dt} - \frac{1}{e}\frac{dJ_e(x)}{dx} = G - \gamma(x)n(x)p(x) \quad (3)$$

Table 1
EA, IP, PL efficiency and PL wavelength of polymers in this work.

Polymer	EA (eV)	IP (eV)	PL efficiency (%)	PL peak wavelength (nm)
BP105	3.0	5.8	30	465
Super-Yellow	3.0	5.4	22	565
PFO	3.0	5.8	40	438
MEHPPV	2.8	4.9	15	587
DPOC10PPV	3.2	5.6	50	496
TFB	2.3	5.3	30	435

$$\mu = \mu_0 \exp\left(\sqrt{\frac{E}{E_0}}\right) \quad (4)$$

where J_e is electron current density, n is the density of electron and p is the density of hole, E is electric field, ε is permittivity of materials, k is Boltzmann's constant, G is the electron–hole pair generation rate, and is the recombination coefficient. We assume G is negligible due to the large band gap of polymers. Eq. (3) describes the net current of electron (holes analogous), combined with drift and diffusion terms. Eq. (4) is Poisson equation. The electron continuity equation, Eq. (5), contains the bimolecular recombination term $\gamma(x)n(x)p(x)$, where γ is in the Langevin form $\gamma = e\mu_m/\varepsilon$ and μ_m is the larger one of μ_e or μ_p. The field-dependent mobility is described as Poole–Frenkel form, Eq. (4), where μ_0 and E_0 are fitting parameters. In this work, we also consider the tunneling current with Fowler–Nordheim (FN) injection:

$$J_{tu} = BE^2 \frac{-8\pi\sqrt{2m^*}\varphi^{3/2}}{3heE} \quad (5)$$

where m^* is the electron effective mass, φ is the energy barrier, h is Planks constant and B is the coefficient that contains the tunneling prefactor and the rate for current backflow. The value of B in Eq. (5) is taken from the fitting data for carrier tunneling from electrodes. [17] Once the energy levels of the polymers and electrodes are known, the carrier mobility can be obtained by fitting the experimental I–V relations of uni-polar devices and the model calculation.
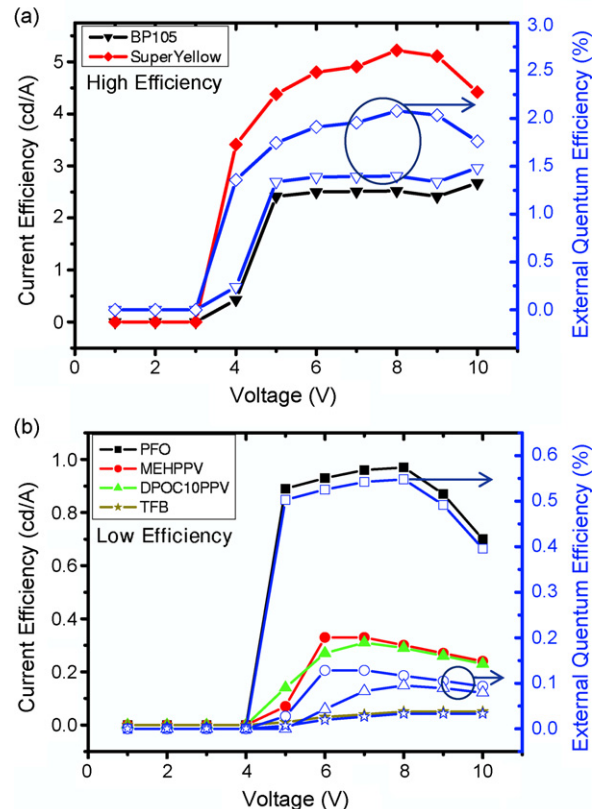
Fig. 2. Current efficiency and external quantum efficiency of polymers in the device structure of ITO/PEDOT/polymer/LiF/Ca/Al. (a) High efficiency polymers, BP105 (down triangle) and Super-Yellow (rhombus) and (b) low efficiency polymers, PFO (square), MEHPPV (circle), DPOC10PPV (up triangle) and TFB (star).
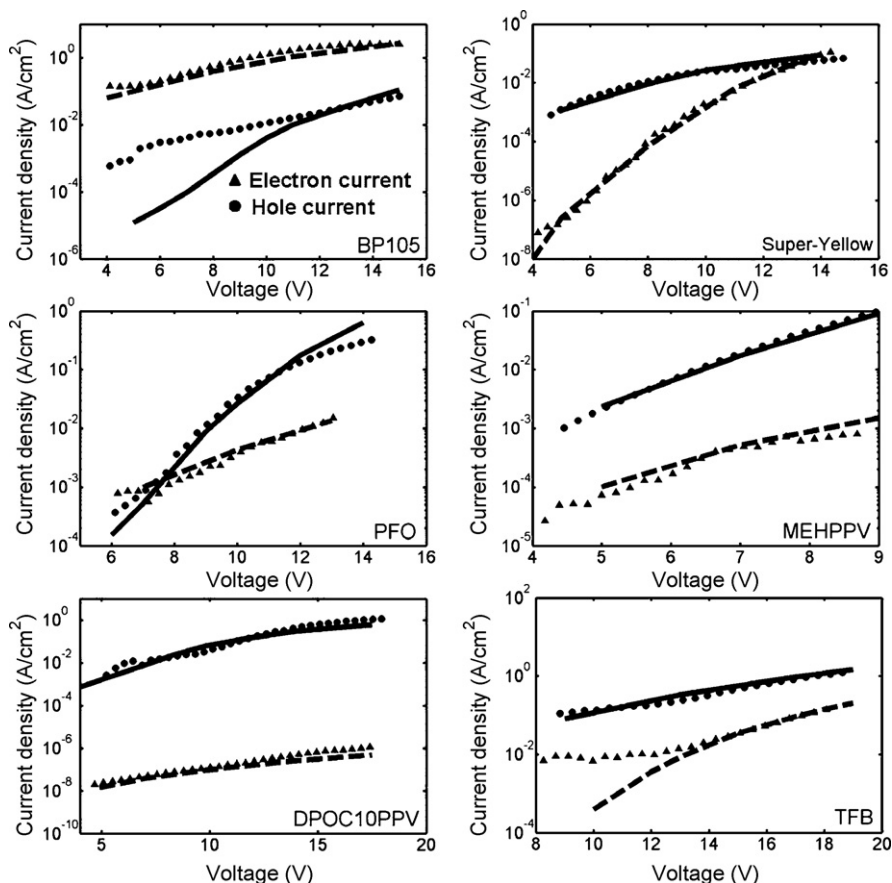
Fig. 3. Comparison of calculated currents and measured currents, including calculated electron currents (dashed line), calculated hole currents (solid line), measured electron currents (solid triangle) and measured hole currents (solid circle).

3. Uni-polar currents, mobility, and pled efficiency

Bipolar device is used to test the EL efficiency of each polymers. Fig. 2 shows the current efficiency. BP105 and Super-Yellow are well-known high efficiency polymers. In fact BP105 is the blue polymer with highest EL efficiency so far, but its PL quantum efficiency is only 30% which is smaller than that of PFO (40%). However, its EL current efficiency is three times larger than PFO at 8 V. In Fig. 2(b), these three polymers all have high PL quantum efficiency, but their EL efficiency is low. Therefore, PL quantum efficiency cannot explain why BP105 and Super-Yellow have such high EL efficiency. To clarify how BP105 and Super-Yellow are special, electron-only and hole-only devices are used to get individual electron and hole currents as functions of voltage and the results are shown in Fig. 3. The hole currents of MEH-PPV, DPOC10PPV, and TFB are all larger than electron currents at least by one order of magnitude. For PFO electron current is slightly larger than hole current at low electric field, but hole current immediately exceeds electron current as voltage increases. Therefore, the hole currents are all far larger than electron currents for all these low EL efficiency polymers under normal PLED operation voltage. However, the electron current is far larger than hole current of BP105 for all voltage range. This is unusual since most polymers are generally p-type resulted from background p-doping in synthesis and other fabrication process, besides electron traps are known to prevail in PLED.6 Although the electron current of Super-Yellow is smaller than hole current at first, it soon catches up at higher voltage. So the remarkable correlation here is that the electron current is larger than or comparable to hole current for high EL efficiency polymers. The uni-carrier cur-

rents are fitted by the previous model to get carrier mobilities, as shown in Fig. 3. The reason for the mismatch of experimental and calculated results at low voltages in BP105 and TFB is possibly that we have not included the trap-assisted tunneling of carriers from the contact into polymers. [18,19] At low electric fields and high barriers, carriers are injected from the contact into localized states in the energy gap and hop to band edge instead of being directly injected into the band edge. This effect becomes insignificant and can be neglected at higher fields. Note TFB has a particularly large electron injection barrier. The fitting at low voltage is not given because there is a linear region caused by the background doping and conducting filament [12] which is not taken into account in the model. The results of calculated mobilities are shown in Fig. 4. In Fig. 4(a), hole mobility is about the same as electron mobility for BP105. For Super-Yellow and TFB electron mobilities approach to hole mobilities at high fields. In Fig. 4(b), hole mobilities are several orders higher than electron mobilities in PFO, MEH-PPV and DPOC10PPV, which indicates that strong carrier imbalance exists in high PL but low EL efficiency polymers. The imbalanced mobility in PFO is consistent with previous reports. [12,13] The current efficiency, quantum efficiency, electron mobility and hole mobility for various polymers are summarized in Table 2.

By comparing with the carrier mobilities with EL efficiencies, the electron transport is shown dominate the EL efficiency rather than high PL quantum efficiency. In the highly efficient polymers, BP105 and Super-Yellow, the carrier mobilities are about the same magnitude at normal operating voltage range. The electron currents are larger than hole currents because of higher hole barrier. Interestingly the carrier mobilities are comparable in TFB, but the
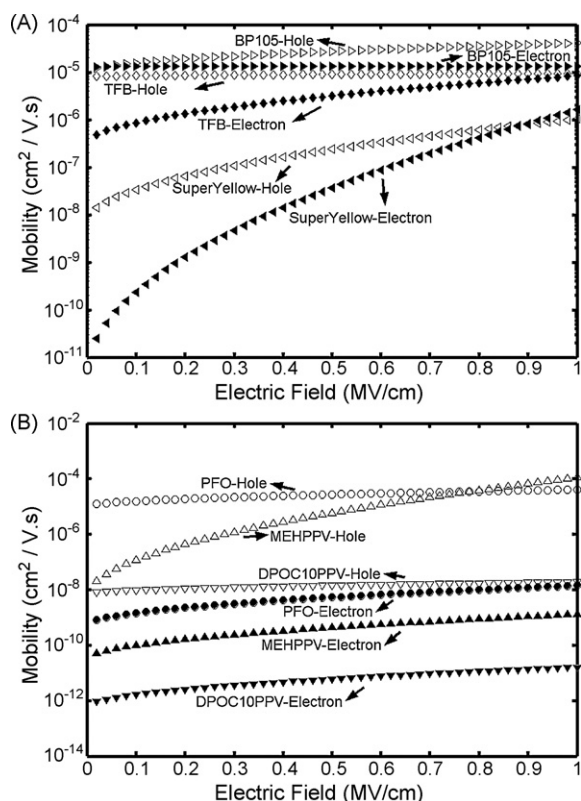
Fig. 4. Fitted electron and hole mobility of polymers. (a) Polymers whose electron and hole mobility are in the same order at normal operating voltages. (b) Polymers whose electron and hole mobility are different at normal operating voltages.

electron barrier is too large for electrons to inject and the EL efficiency is low. In general the electron currents are more crucial than hole currents. For the low efficiency polymers, PFO, MEH–PPV and DPOC10PPV, hole mobilities are several orders of magnitude higher than electron mobilities. The mobility difference yields the carrier imbalance in device and gives low EL efficiency. As the above discussion goes, there are two conditions to achieve high EL efficiency, high electron mobility and low electron barrier.

Even though the uni-polar devices provide useful comparisons between the electron transport properties of different materials, the electron and hole currents in Fig. 3 cannot be simply summed up to give the total current in the bipolar LED. In general the bipolar current is very different from the sum of the two uni-polar currents experimentally. The electron or hole current is determined by the effective injection barrier, the electric field distribution, as well as the mobility. All the three factors are strong functions of the space charge distribution which is in turn determined by the presence of the carriers with the opposite charge. The barrier is lowered by the image-charge effect and the mobility depends on both the field exponentially and the energy disorder caused by the opposite charge [20]. For example, in Fig. 3 the electron current for

Super-Yellow is small at low voltage in uni-polar device. In bipolar LED, the electron current can be much higher because of the presence of the holes will screen the field near the anode and cause a much higher field near the cathode. Because of the strong dependence of the electron mobility on the field as shown in Fig. 4, the electron current in LED can be much higher than the uni-polar current at a given voltage to achieve good balance. For PFO, there is a large hole injection barrier. The hole current therefore depends sensitively on the field near the anode due to image force barrier lowering. In LED the field could be much higher due to the screening near the cathode, the hole current is therefore expected to be much larger than shown in Fig. 3 and dominate the electron current.

4. Discussion

The purity of polymer is very important in getting high electron mobility. Many impurities play the role of electron traps, including inorganic impurities Cl, Na, K or organic impurities induced in synthesis process and even end-groups of polymers and absorbed molecular oxygen. [14,21] For BP105 bipolar device the electron current is free of such obstacles [14], as suggested by the larger electron current than hole current shown in uni-polar devices. In addition to low cathode injection barrier, high purity, large molecular weight, and air stability for BP105 and Super-Yellow are believed to be responsible for the desired high electron current and high efficiency.

In addition to charge transport and PL quantum efficiency there are a few other factors which might also influence the EL efficiency. There has been reports that the singlet exciton formation probability is higher than 1/4 in some polymers [22,23]. Recent experiments suggest that the probability is 1/4 as the case of small molecules [24,25]. The issue of singlet/triplet (S/T) ratio remains under debates to date. In this paper the singlet exciton formation probability is assumed to be 1/4 of the studied materials, thus the difference in EL efficiency is not due to the exciton spin consideration. The results and conclusions would be impacted if the probability is other than 1/4. The cathode quenching of the excitons is known to reduce the EL efficiency at low voltage when the recombination zone is close to the metal cathode due to the low electron mobility. However at normal operation voltages above 4 V the recombination zone becomes rather homogeneous throughout the film thickness [26]. Since the comparison of the efficiencies of the devices is based on its maximal value at higher voltage the difference in the cathode quenching is not expected to have a major effect. Similarly due to the homogeneous recombination zone the difference in the light out-coupling efficiency can be neglected. The importance of electrode quenching also depends on the exciton diffusion length which in turn depends on the exciton lifetime. For polymers with particularly long lifetime there might be an enhanced quenching effect. Transient photoluminescence experiments however see no major difference in the exciton lifetime. Indeed most of the luminescent polymers have lifetime around 0.5 ns [27,28].

Table 2
Maximal current efficiency, external quantum efficiency (EQE) and corresponding electron and hole mobility of polymers in this work.

Polymer	Maximal current efficiency (cd/A)	EQE (%)	Electron mobility (cm^2/V s)	Hole mobility (cm^2/V s)
BP105	2.67 (at 10 V)	1.48	4.1×10^{-5}	1.3×10^{-5}
Super-Yellow	5.22 (at 8 V)	2.08	4.1×10^{-7}	6.1×10^{-7}
PFO	0.97 (at 8 V)	0.55	1.4×10^{-8}	4.1×10^{-5}
MEHPPV	0.33 (at 7 V)	0.13	7.1×10^{-10}	2.2×10^{-5}
DPOC10PPV	0.31 (at 7 V)	0.08	9.3×10^{-12}	1.6×10^{-8}
TFB	0.05 (at 8 V)	0.03	9.2×10^{-6}	5.9×10^{-6}

5. Conclusion

For high PL efficiency polymers, the electron current is demonstrated to be the most important factor to determine the EL efficiency. The universal features to get higher EL efficiency are that the carrier mobilities need to be in the same order and, more importantly, the electron currents are larger than hole currents. To get larger electron currents, the purity of polymer is significant and the electron injection barrier should not be too high. This is a direction not only for chemists to design high-purity polymers but also for physicists to design proper device structure in balancing electron and hole currents.

Acknowledgements

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