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Electron mobility and electroluminescence efficiency of blue conjugated polymers

Chia-Ming Yang [a], Hua-Hsien Liao [a], Sheng-Fu Horng [a], Hsin-Fei Meng [b,*],
Shin-Rong Tseng [b], Chain-Shu Hsu [c]

[a] *Department of Electric Engineering, National Tsing Hua University, Hsinchu 300, Taiwan, Republic of China*
[b] *Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China*
[c] *Department of Applied Chemistry, National Chiao Tung University,*
Hsinchu 300, Taiwan, Republic of China

Abstract

We study systematically the underlying property which determines the electroluminescence efficiency of blue polymers based on polyfluorene and its copolymers. The photoluminescence efficiency is high (40–50%) for all the selected polymers, but the electroluminescence efficiency varies in a wide range. The hole mobility is measured by transient electroluminescence. The electron mobility is obtained from the current in electron-only device using space-charge-limited current equation. All polymers share roughly the same results, whereas electron mobility is the critical factor for electroluminescence. In general, low efficiency results from the low electron mobility.
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Solution-processed polymer light-emitting diode (PLED) have a great potential for many low-cost and large area display applications, for example in the emissive pixels or backing light of the liquid crystal display. In order to achieve full-color blue light is the most critical. Green and red light can be obtained from blue light either using color converter externally or using dopants in the polymer host internally. So far, the red and green PLED have high efficiency, while the blue PLED is falling behind. Furthermore, for the blue polymer with relatively high efficiency, like LUMATION* BP105 developed by the Dow Chemical Company, the chemical structure is not available and the material has to meet stringent conditions and is difficult to synthesize in large scale with low cost. For other blue polymers based on polyfluorene and copolymers with known chemical structure and easier synthesis, the PLED efficiency is much lower. It is therefore vital to understand the microscopic properties which determines the efficiency and reveal the correlation between these properties and the chemical structures.

Interestingly, the photoluminescence (PL) quantum efficiency is high for some blue polymers with very poor PLED efficiency. High PL efficiency means the excitons are easy to emit light, but the performance of LED is limited also by the charge transport and exciton formation. For all the blue polymers the ionization potential (IP) is around 5.8 eV. With similar energy gap, the electron affinity (EA) is expected to be similar to one another and located around 2.8 eV. Charge injection from the lower work function cathode is not expected to be the main factor to determine the efficiency. Charge carrier mobility is therefore likely to underlie the observed difference in efficiency. Surprisingly, even through the carrier mobility of poly(*p*-phenylene vinylene) (PPV) derivatives have been studied extensively [1,2], no such study was performed for polyfluorene especially for the electron part.

In this paper, we compare the hole as well as the electron mobility for a selection of blue polymers based on polyfluorene (PF) and copolymers. The hole mobility is measured by the transient electroluminescence (EL) method [4–6], while the electron mobility by the space-charge-limited current (SCLC) fitting. It turns out that the hole mobility of all the polymers are about the same, but the electron mobility differs by several

* Corresponding author. Tel.: +886 5731955.
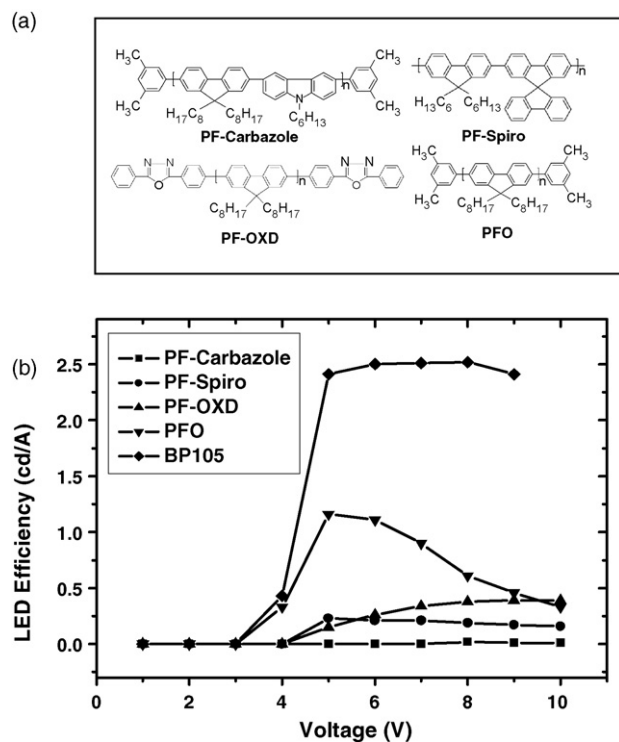*E-mail address:* meng@mail.nctu.edu.tw (H.-F. Meng).

Fig. 1. (a) The chemical structure of four PF-derivatives. (b) The EL efficiency of the PLED as function of driving voltage.
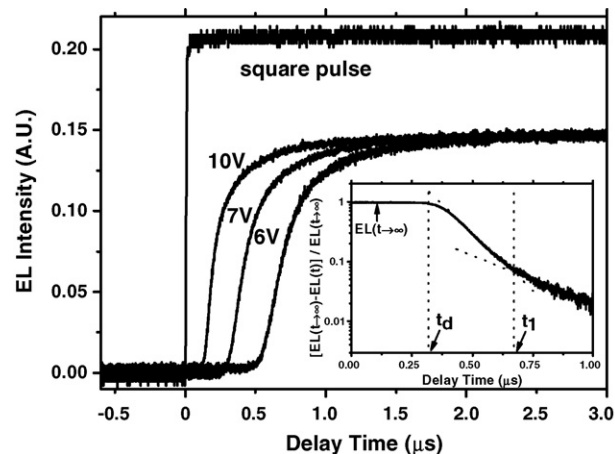

Fig. 2. The response signal is the PFO LED emission at 8 V square pulse, and the synchronized signal is the applied pulse. The device is ITO/PEDOT/PFO/Ca/Al. The delay time t_1 is indicated in the insert and the detailed description are shown in Ref. [3].

orders of magnitude. More importantly, there is a direct correlation between the electron mobility and the LED efficiency. Good electron transport is therefore identified as the single most important property for a high-efficiency blue PLED.

Four PF derivatives are studied: poly(9,9-dioctylfluorenyl-2,7-diyl) end capped-with dimethylphenyl (PFO), poly(9,9-dioctylfluorenyl-2,7-diyl) end capped-with 2,5-diphenyl-1,2,4-oxadiazole (PF-OXD), poly[(9,9-dihexylfluorenyl-2,7-diyl)-alt-co-(9,9'-spiro-bifluorene-2,7-diyl)] (PF-Spiro), and poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(9-hexyl-3,6-carbazole)] end capped-with dimethylphenyl (PF-Carbazole). The materials are purchased from American Dye Source. The chemical structures are shown in Fig. 1(a). BP105 from the Dow Chemical Company with unknown structure is also inducted for comparison. The polymers are dissolved in toulene and LEDs are fabricated on indium tin oxide (ITO)-coated glass substrate. The 50 nm hole injection layer poly(3,4-ethylene dioxythiophene) doped by poly(styrene sulphonate) (PEDOT:PSS) is spin-coated. On top of that the PF derivatives are spin-coated as the emissive layer with thickness of 100 nm. The cathode is calcium (35 nm)

capped with aluminum (100 nm). The active area is 4 mm². The LED characteristics are shown in Fig. 1(b). PL efficiency is measured for thin film spin-coated on the glass substrate. The photo-excitation source is 405 nm laser, and the fluorescence is collected by an integration sphere to obtain the absolute PL quantum efficiency. The PL and maximal EL efficiency are shown in Table 1. The remarkable feature is that while the PL efficiencies are all around 40%–50%, the EL current efficiency differ by as large as 100 times. They can be roughly grouped as poor (PF-Carbazole), intermediate (PF-Spiro, PF-OXD, PFO), and good (BP105). Mobility measurement is performed to reveal the origin of such difference.

The hole mobility is measured by the transient EL under electric pulse. As a square voltage pulse is applied to the LED, there is a delay between the pulse and the rise of the light emission because the carriers need to move across the emissive layer to recombine. The delay is mainly determined by the time which the faster carriers take to move across the whole thickness. Hole is known to be the faster carrier in PF derivatives [3]. The EL delay can be therefore used to get the hole drift velocity and consequently the mobility with known electric field. The LED is driven by a function generator (Agilent 33220A) with 35 ns rise time. The repetition rate is 50 KHz, and the driving voltage operates from 5 to 10 V. The temporal evolution of the light output is measured by a photomultiplier tube (Hamamatsu R3256) with 31 ns delay time and 3.4 ns rise time. The overall response time of the instrument is 20–30 ns. The response waveform of

Table 1
The PL and EL efficiency of four PF-derivatives and BP105 are compared

Polymer	PF-Carbazole	PF-Spiro	PF-OXD	PFO	BP105
PL efficiency (%)	36.8	34.6	56.2	45.0	40.5
Maximum EL efficiency (cd/A)	0.02	0.23	0.40	1.16	2.52
EL EQE (%)	0.01	0.16	0.38	0.82	1.50
EL λ_{max} (nm)	425	425	432	435	470

EQE is external quantum efficiency. λ_{max} is the peak wavelength of EL spectrum. The LED structure is ITO/PEDOT(50 nm)/PF(100 nm)/LiF(2 nm)/Ca(35 nm)/Al(100 nm), and the PL sample structure is Glass/PF/Glass.
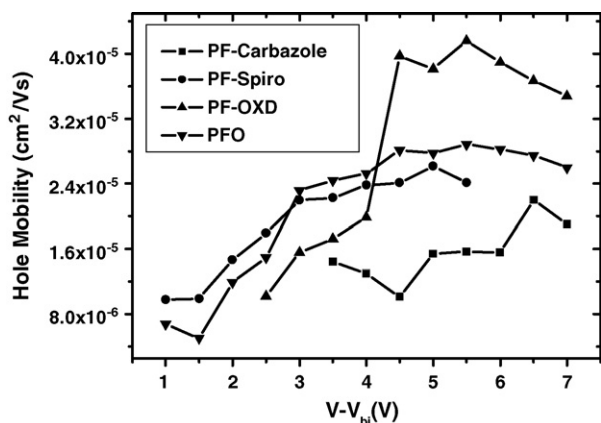
Fig. 3. The hole mobility versus driving voltage of four PF-derivatives.

the PLED output and the synchronized pulse signal are shown in Fig. 2. t_1 is the rise time and the hole mobility μ_h is given by $\mu_h = L^2/t_1(V - V_{bi})$. L is the emissive layer thickness, V is the driving voltage, and $V_{bi}=2.2$ V is the build-in voltage (the work function difference between two electrodes). The rise time t_1 shown decreases as the voltage increases as expected. The resulting hole mobility is shown in Fig. 3. The mobility increases slightly with the driving voltage and saturates at the high electric field. The hole mobility of PFO is similar to the earlier reports [3,6]. The hole mobility of BP105 has been previously measured to be about 10^{-5} cm^2/Vs. The differences among all the polymers are no greater than a factor of three. We cannot assort the EL efficiencies in Table 1 by the hole mobility. It is evident that the hole mobility is not the distinguishing property of these polymers and dose not dictate the LED efficiency. We therefore search for the decisive factor in electron mobility.

In principle, it is possible to obtain the mobility of the slower carrier (electron) from the long-time transient of EL in the millisecond scale. Such approach is not very reliable because of the initial spike in the waveform when the pulse width is too wide [7,8]. For this reason, we measure the electron mobility μ_e by the current-voltage relation of the electron-only device [9], with structure ITO/Ag/polymer/Ca/Al. Because that the electron injection barrier between Ca with workfunction 2.9 eV and polymers with EA 2.8 eV is small. The electron current is expected to be bulk-limited instead of injection-limited as in the case of hole current, where the injection barrier from PEDOT is around 0.8 eV. The bulk-limited current is governed by the SCLC equation $J_{SCLC} = 9/8\varepsilon\mu_e(V - V_{bi})^2/L^3$. J is the current, ε is the permittivity of the polymer, μ_e is the electron mobility, V is driving voltage, V_{bi} is the built-in potential, and L is the polymer thickness. Fig. 4(a) shows the I–V curves of the blue polymers in log–log scale. We see the slope approaches two as predicted from SCLC. Unlikely the hole transport, these four polymers have huge difference in electron transport. BP105 has the highest electron current, the second is PFO, the third PF-OXD, the fourth PF-Spiro, and the lowest is PF-Carbazole. The current density distribution ranges from 10^{-2} to 10^2 mA/cm^2 at 10 V. Using SCLC relation we calculate electron mobility μ_e [10], which is shown in Fig. 4(b). Strikingly, as one compares Fig. 4(b) and Table 1 the order of the electron mobility turns
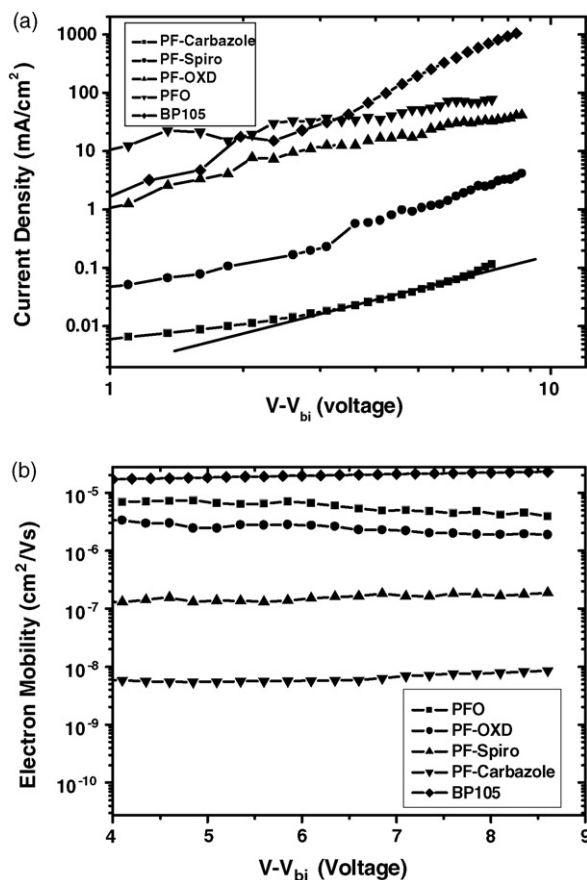

Fig. 4. (a) The electron-only current in ITO/Ag/Polymer/Ca/Al device of the polymers. The line is of slope 2. (b) The electron mobility obtained by fitting the curves in (a) by SCLC relation for different polymers are shown.

out to be exactly the same as the EL efficiency. The high efficiency BP105 possesses μ_e higher than 10^{-5} cm^2/Vs, while μ_e of the low efficiency PF-Carbazole is only 1.0×10^{-8} cm^2/Vs. Note the current–voltage relation in Fig. 4 follows the quadratic relation surprisingly well for voltage over 3 V. The quadratic relation holds only in a trap-free regime [11], implying that the electron transport is not dominated by deep traps in the blue PLED despite of the low carrier mobility.

From the exact correlation for these five polymers, we conclude that the origin of low EL efficiency in blue polymers is low electron mobility, despite of the high PL efficiency and comparable hole mobility. It is remarkable that such major difference in μ_e exists in the family of PF-based polymers. We do not consider it results mostly from extrinsic causes like doping, impurity, or other perturbation of the environment [12]. The fabrication procedure is all the same and the molecular weight and purity are similar, so the difference is more likely to be on the intrinsic chemical structure. The electron mobility is higher for polymers whose main chain contains only fluorene repeating unit, like PFO and PF-OXD, where the hole and electron mobility are more comparable and the LEDs are more charge balanced. The OXD end capper appears to act as traps and reduce the electron mobility. If the main chain is composed of different moiety (like spiro-fluorene and carbazole), the electron mobility becomes much lower and have a rather poor EL efficiency.

The carbazole and spiro-fluorene moiety in the main chain may hinder the backbone packing and cause more energy disorder for electron transport. Charge balance is required to achieve d high efficiency in LED. Most of the polyfluorene blue polymers have reasonable hole transport property, yet it remains a challenge to realize high electron mobility except for BP105. The wide gap and relatively small EA imply the sensitivity of electrons to defects and disorder which could easily cause shallow electron traps states in the gap. In addition to reducing the electron mobility and the charge balance, the traps may act a non-radiative recombination centers during electroluminescence.

Among all the five polymers, only PFO electron mobility has been reported [3]. Using transient EL, PFO μ_e is measured to be around 10^{-7} cm^2/Vs, much smaller than the $10^{-6}$to 10^{-5} cm^2/Vs measured here by SCLC. This is probably because the electron traps are filled in SCLC but not in transient EL due to much lower carrier density in the transient [13,14]. In fact, it is impossible to get μ_e by time-of-flight method presumably due to more active electron traps at the still lower electron density. Indeed, carrier mobility in disordered semiconductors has been reported to depend sensitively on the carrier density. In terms of carrier density, SCLC method is more relevant to the working PLED in steady state compared with the transient EL and TOF method. In fact, SCLC proves to be the only successful way so far to compare the electron transport in blue polymers systematically.

In conclusion, we study the hole and electron mobility systematically for blue polymers with EL efficiency ranging from 2.5 to 0.02 cd/A. The hole mobilities are almost the same, while the electron mobility differ by more than three orders of magnitude and show exact correlation with the EL efficiency. High electron mobility is therefore identified as the key to efficient blue PLED. In addition to extrinsic effects like impurities, the chemical structure plays an deciding role to the electron mobility.

Acknowledgements

References

[1] D. Hertel, H. Bässler, U. Scherf, H.H. Hörhold, J. Chem. Phys. 110 (1999) 9214.
[2] P.W.M. Blom, M.C.J.M. Vissenberg, Mater. Sci. Eng. R-Rep. 27 (2000) 53.
[3] D.J. Pinner, R.H. Friend, N. Tessler, J. Appl. Phys. 86 (1999) 5116.
[4] D.J. Pinner, R.H. Friend, N. Tessler, Appl. Phys. Lett. 76 (2000) 1137.
[5] D. Poplavskyy, W. Su, F. So, J. Appl. Phys. 98 (2005) 014501.
[6] A.J. Campbell, D.D.C. Bradley, J. Appl. Phys. 89 (2001) 3343.
[7] V. Savvate'ev, J. Friedl, L. Zou, W.J. Oldham, J. Shinar, Appl. Phys. Lett. 76 (2000) 2710.
[8] C.W. Ma, O. Lengyel, J. Kovac, I. Bello, C.S. Lee, S.T. Lee, Chem. Phys. Lett. 397 (2004) 87.
[9] P.W.M. Blom, M.J. de Jong, M.G. van Munster, Phys. Rev. B 55 (1997) 656.
[10] H. Campbell, D.L. Smith, Solid State Physics, vol. 55, Academic, San Diego, 2001.
[11] K.C. Kao, W. Hwang, Electric transport in solids with particular reference to organic semiconductors, Pergamon, Oxford, 1981 (Chapter 3).
[12] W. Wu, M. Inbasekaran, M. Hudack, D. Welsh, W. Yu, Y. Cheng, C. Wang, S. Kram, M. Tacey, M. Bernius, R. Fletcher, K. Kiszka, S. Munger, J. O'Brien, Microelectron. J. 35 (2004) 343.
[13] C. Tanase, P.W. Blom, D.M. de Leeuw, Phys. Rev. B 70 (2004) 193202.
[14] W.F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P.A. Bobbert, P.W.M. Blom, D.M. de Leeuw, M.A.J. Michels, Phys. Rev. Lett. 94 (2005) 206601.