

Flexible organic light emitting diodes (OLEDs) based on a blue emitting polyfluorene

M. Vasilopoulou^{*1}, L. C. Palilis^{*1}, A. Botsialas¹, D. G. Georgiadou¹, P. Bayiati¹, N. Vourdas¹, P. S. Petrou², G. Pistolis³, N. A. Stathopoulos⁴, and P. Argitis¹

¹ Institute of Microelectronics, NCSR “Demokritos” 153 10 Athens, Greece

² Immunoassay Laboratory, I/R-RP, NCSR “Demokritos” 153 10 Athens, Greece

³ Institute of Physical Chemistry, NCSR “Demokritos” 153 10 Athens, Greece

⁴ Department of Electronics, Technological and Educational Institute of Pireaus, Aegaleo 12244, Greece

Received 30 November 2007, revised 22 May 2008, accepted 27 May 2008

Published online 24 September 2008

PACS 78.60.Fi, 78.66.Qn, 85.60.Jb

* Corresponding authors: e-mail mariva@imel.demokritos.gr, lpalil@imel.demokritos.gr, Phone: +30 210 6503269, Fax: +30 210 6511723

Flexible OLEDs were demonstrated using a highly efficient blue electroluminescent polyfluorene derivative. The flexible devices were fabricated on indium tin oxide (ITO) coated polyethylene terephthalate (PET) substrates with a sheet resistance of 35 Ω per sq. The emitting layer was poly[9,9-di-(2'-ethylhexyl)fluorenyl-2,7-diyl] (PF). A significant improvement of the luminance and device efficiency was achieved by confining the exciton formation zone within PF by two wide band-gap materials, namely PVK as a hole transport layer (HTL) and an inorganic oxide layer (IOL) as an electron transport and hole blocking layer. In order to achieve full-color LEDs based on a common host material,

we probed the use of suitable dye emitters dispersed in PF at appropriate concentrations. The selection of the emitters is based on their capability to be effective energy transfer acceptors from the blue emitting PF. In particular, energy transfer was demonstrated from blue to green for PF-doped with the green dye emitter 1-[4-(dimethylamino)phenyl]-6-phenylhexa-1,3,5-triene (DMA-DPH), and from blue to red for PF-doped with the red dye emitter (4-dimethylamino-4'-nitrostilbene) (DANS). This demonstration paves the way for developing highly efficient blue, green and red flexible OLEDs based on a common blue emitting PF host.

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction

In the last few years, electronic devices such as flexible organic light emitting diodes (OLEDs) have attracted considerable interest for use in the next generation flat panel displays and solid state lighting, because of their light weight, robustness, and compatibility with roll-to-roll processes [1, 2]. Flexible devices are generally constructed on plastic films, like polyethylene terephthalate (PET), which are superior in flexibility, formability and transparency. Because OLED performance is strongly affected by carrier injection, it is imperative to use a high quality anode layer with low resistance, high transparency and high work function as an Sn-doped In_2O_3 (Indium Tin Oxide, ITO) film deposited on PET flexible substrate. Interface engineering between the anode and the emitting layer is important for the improvement of the device lifetime as well as luminance efficiency. Previous literature reports

described several approaches to interface engineering that resulted in improving the device performances, for instance the anode modification by plasma treatment [3], introduction of a hole injection layer (HIL) [4] and/or a hole transporting interlayer between the HIL and the emitting layer [5]. As an air-stable cathode electrode, aluminum has been commonly used for OLEDs due to its relatively low work function (4.3 eV) and high reflectivity.

In order to achieve red-green-blue (RGB) emission for application in the next generation of flat-panel displays, efficient and stable saturated blue emission is required and, thus far, remains the main challenge. Polyfluorene (PF) derivatives are among the most promising blue-emitting materials because of their high photoluminescence (PL) quantum yield and their pure well-structured blue emission [6–8].

Here, we report single and multilayer blue PLEDs based on a PF derivative on plastic (PET) substrates that exhibit good performance characteristics when operating in air without any encapsulation. We demonstrate that an exciton-confining multilayer PLED structure can result in higher luminance and improved luminous efficiency as well as stability. We also show that by doping suitable green and red dye emitters in a blue PF host, energy transfer to the green and red can be achieved paving the way for fabrication of RGB flexible LEDs based on a universal blue PF host.

2 Experimental

2.1 Materials and instrumentation Fluorescent dyes 1-(4'-dimethyl-aminophenyl)-6-phenyl-1,3,5-hexatriene (DMA-DPH), and 4-dimethylamino-4'-nitrostilbene (DANS) were purchased from FLUKA. Poly[9,9-di-(2'-ethyl-hexyl)fluorenyl-2,7-diyl] (PF) and Poly(9-vinylcarbazole) (PVK) were purchased from American Dye Source and Aldrich, respectively, and used with no further purification. Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was purchased from Aldrich. In Fig. 1, the chemical structure of the PF polymer and the dyes used in this work are shown.

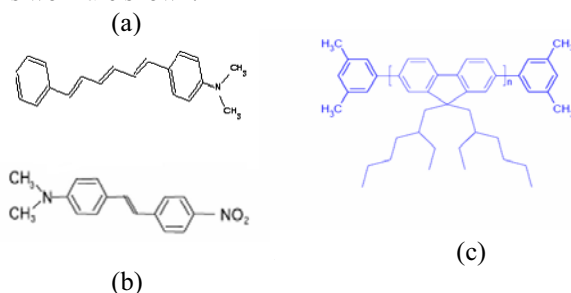


Figure 1 Chemical structures of (a) DMA-DPH, (b) DANS and (c) PF.

For absorption spectra a Perkin-Elmer Lambda-16 U/Vis spectrophotometer was employed while PL spectra were recorded with a Perkin-Elmer LS-50B PL spectrometer.

2.2 PLED fabrication and characterization

Two sets of PLEDs were fabricated on ITO coated polyethylene terephthalate (PET) substrates (with an ITO resistance of 35 Ω/sq). a) Single-layer devices with a PF emitting layer that was spun at 2000 rpm and then baked at 80 $^{\circ}\text{C}$ for 5 min from a 20mg/ml toluene solution. b) Exciton-confining three-layer devices with wide-band gap 40 nm PVK and 30 nm IOL (termed inorganic oxide layer) films that were spin coated from orthogonal solvents (to avoid layer interdiffusion), as a hole (prior to PF) (HTL) and electron (on top of PF) transport/hole blocking layer (ETL/HBL), respectively. By sandwiching the PF emissive layer between two wide-band gap (>3 eV) HTL and ETLs, carrier and exciton confinement can be achieved. ITO coated PET substrates were precleaned in an ultrasonic

bath with a sequence of DI water, acetone, isopropanol and treated with oxygen plasma for 5 min to improve the ITO properties. A 40 nm thick film of PEDOT-PSS was spin coated (at 4000 rpm and baked at 120 $^{\circ}\text{C}$ for 30 min) on top of ITO in order to improve hole injection and substrate smoothness and enhance the performance of the PLEDs. Device fabrication was completed with a 250 nm thick aluminum cathode electrode which was deposited on top of the organic film by thermal evaporation under high vacuum. All the fabricated devices have an active area of 12.56 mm^2 . In Fig. 2, a representative exciton-confining three-layer blue PLED structure fabricated here is shown.

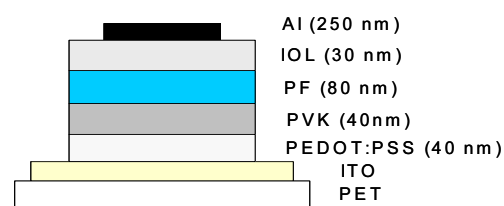


Figure 2 Representative exciton-confining 3-layer device structure used in this work.

Current density-voltage (J-V) measurements were obtained using a programmable Keithley 230 Voltage Source and a 195 A Multimeter. Luminance measurements (in forward direction) and electroluminescence (EL) spectra were recorded simultaneously using a USB 2000-UV-Vis miniature fiber optic spectrometer. All measurements were carried out at room temperature under ambient atmosphere without any encapsulation.

3 Results and discussion

In Fig. 3, the PL spectrum as well as the evolution of the EL spectra with increasing applied electric field are shown.

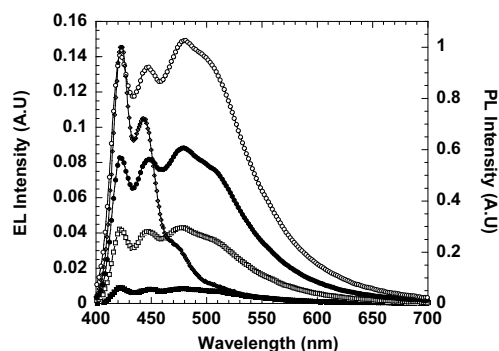


Figure 3 PL spectrum of PF (open diamonds) and EL spectra of a 3-layer flexible PF-based PLED with increasing applied electric field [0.53 MV/cm (filled squares), 0.93 MV/cm (open squares), 1.5 MV/cm (filled circles) and 2.1 MV/cm (open circles)].

The PL spectrum of PF shows an emission maximum at 420 nm with vibronic replica at 445 nm (peak corre-

sponding to the 0-1 transition) and 480 nm (shoulder corresponding to the 0-2 transition) and a FWHM of around 40 nm, typical of a rigid backbone polyfluorene [6]. Two are the noteworthy characteristics of the EL spectra. First, although the two main EL peaks appear at 420 nm and 445 nm (in identical positions as in PL), the 0-1 transition peak (at 445 nm) and the 0-2 transition shoulder of the PL (at 480 nm) show a significant enhancement in their relative weight in the EL. Second, the EL spectrum broadens considerably and shows a long wavelength tail, which is absent in the PL, that extends to 550-600 nm resulting in the color of the PLED appearing cyan blue to the unaided eye. There is also a slight increase in the relative weight of the emission band at 480 nm as the electric field increases. The difference between the EL and the PL spectra and, in particular the growth of the 0-1 and 0-2 PL features to dominant EL peaks, particularly at large electric fields, may be assigned to either interference effects, the formation of excimers or, as recently suggested [9], emission from exciton trapping keto-defect sites on the PF backbone resulting in undesired green emission (the so-called “g” band) and device degradation. Various PF derivatives have shown the appearance of blue-green EL emission under bias operation that has been proposed to originate from electro-oxidation of fluorenone keto-defect sites on the polymer backbone upon application of an external field [9]. We first note that both single layer and exciton confining device structures showed similar EL spectra (not shown here) which suggests that interference effects due to the distance dependence of the emission zone from the cathode may not play a significant role in these devices. Now, in order to examine the photooxidative stability of the PF polymer, we have performed a) annealing of a 100 nm PF film at 150 °C in air for 5 hours and b) continuous UV irradiation (illumination $\lambda_{\text{max}} = 254$ nm) of the same film in air for 1 hour. We noticed that there was almost no change in the UV-vis absorption, PL spectrum, color and efficiency of PF which demonstrates its excellent photostability. We therefore tentatively attribute the difference in EL to electro-oxidative degradation of the backbone under an applied electric field as reported for other PF derivatives [9].

In Figs. 4 and 5, a comparison of the current density and luminance versus voltage characteristics for devices with a single PF layer and an additional IOL ETL and a PVK HTL are shown.

The 3-layer exciton confining PLED shows lower leakage current by one order of magnitude at low electric fields (below turn-on) while the onset of current injection and light emission (turn-on field) decreases, as expected. The current density flow and particularly the luminance are significantly enhanced at a given electric field. The addition of the HTL and ETL results in two additional interfaces (with PF) being created where charge accumulation may occur leading to redistribution of the internal electric field and therefore to enhanced injection from the electrodes and an enhanced probability of holes and electrons to cross the HTL/PF and ETL/PF barriers and enter the ad-

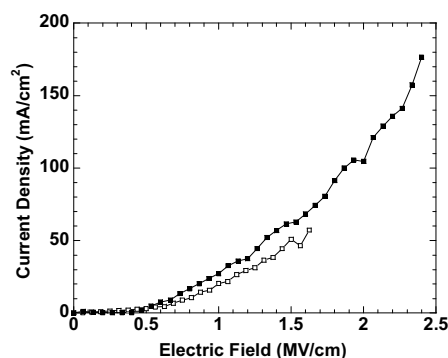


Figure 4 Current density versus voltage characteristics for devices with a single PF layer (open squares) and with an additional IOL ETL and a PVK HTL (filled squares).

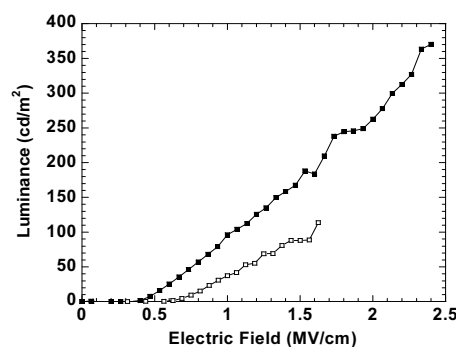


Figure 5 Luminance versus voltage characteristics for devices with a single PF layer (open squares) and with an additional IOL ETL and a PVK HTL (filled squares).

jacent PF emissive layer facilitating more efficient exciton formation [10]. A maximum luminance of 380 cd/m^2 was obtained in the 3-layer PLED compared to only 120 cd/m^2 for a single PF layer PLED (an improvement of a factor of 3). The device could also be driven to a higher electric field and withstood larger current densities (by a factor of 3) without breaking down. These are attributed to the improved electron injection from Al to the IOL and then to the LUMO of PF (by lowering the electron injection step at each interface), to the high electron mobility of the IOL and to the effect of the exciton-confining structure that confines the recombination zone further away from the Al cathode minimizing exciton diffusion and quenching. In Fig. 6, the EL luminous efficiency as a function of current density for these devices is shown.

The EL luminous efficiency reached 0.35 cd/A for a 3-layer PLED compared with 0.2 cd/A for the control single layer PLED. This modest enhancement by almost a factor of 2 indicates improved charge balance and increased exciton formation (more efficient recombination) caused by the enhanced electron injection and the hole blocking effect at the Al/IOL interface, the reduced exciton quenching near the cathode interface and the large barrier that both electrons and holes have to overcome in order to cross the

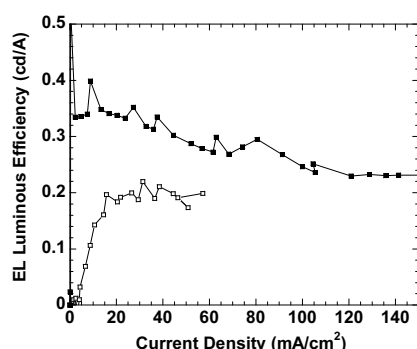


Figure 6 EL luminous efficiency as a function of current density for devices with a single PF layer (open squares) and an additional IOL ETL and a PVK HTL (filled squares).

HTL/PF and ETL/PF interfaces and leak to the HTL and ETL, respectively. This can be understood if we reasonably assume that holes are the majority-type carriers injected in the PF PLED (due to the higher hole mobility of PF and the large barrier for electron injection from Al to the LUMO of PF) [11] and that electron injection and/or transport should be the limiting factor in device performance. In Fig. 7, a photograph of a flexible blue OLED on PET upon bending is shown during operation in air (under standard laboratory conditions). We note that the device could be easily folded (by bending the PET substrate up to a few mm in radius) without appreciable loss of luminance. These devices also operated in air for up to 6 hours (in constant voltage mode) without significant changes in the device characteristics, except a small decrease in luminance (up to 20%) and a corresponding decrease in the device efficiency.



Figure 7 Photograph of a flexible blue OLED upon bending.

We further tested the suitability of PF as a universal conducting host for obtaining green and red emission by doping in it a suitable green and red emitter. In particular, the green dye emitter DMA-DPH and the red DANS, were both mixed in the PF matrix and, in Fig. 8, the absorption spectra of both dye emitters together with the PL spectra of PF and the green and red dye-doped (in a molar ratio 2:1) PF films are shown.

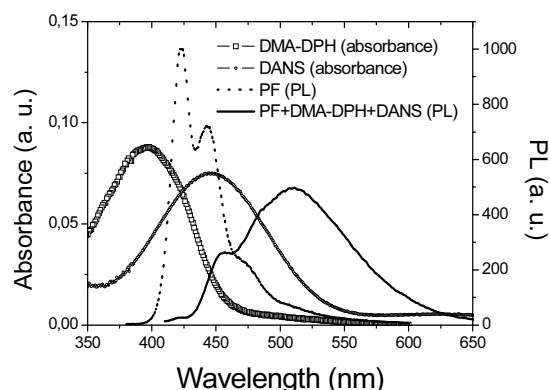


Figure 8 Energy transfer from PF to DMA-DPH and DANS.

Dyes' absorption spectra are dominated by broad featureless bands centered at ~390 and 445 nm for DMA-DPH and DANS, respectively, while the PL of PF shows a maximum at 420 nm and vibronic shoulders at 445 and 480 nm. Quite efficient excitation (Förster-type) energy transfer [12] was found to take place from PF to the dye molecules due to the relatively large overlap of PF's emission and each dye's absorption spectra (extending from 400 to 550 nm). The PL spectrum of the DMA-DPH/DANS PF doped film is dominated by a peak at ~510 nm (characteristic of DMA-DPH's PL) and a shoulder at ~455 nm (due to residual PF emission), but with only a small contribution from the PF main PL peak at 420 nm.

4 Conclusion

In summary, we have realized efficient and bright blue EL from a PF derivative based PLED on a flexible PET substrate that operates in air without performance deterioration when substrate bending was applied. Further improvements in performance may be realized by utilizing a more efficient cathode, incorporating a higher mobility HTL and optimizing the thickness of the various layers. We also demonstrated energy transfer from the blue PF host to green and red dyes used as guest molecules. This opens the way for fabricating flexible RGB PLEDs by using a universal conducting blue host polymeric material.

Acknowledgements This research has been conducted within the framework of "Archimedes: Funding of research groups in TEI of Piraeus" project, co-funded by the European Union (75%) and the Greek Ministry of Education (25%).

References

- [1] G. Gustafsson, Y. Cao, G. M. Treasy F. Klavetter, N. Colaneri, and A. Heeger, *Nature* **357**, 477 (1992).
- [2] H. Kim, G. S. Horwitz, G. P. Kushto, Z. H. Kafafi, and D. B. Chrisey, *Appl. Phys. Lett.* **79**, 284 (2001).
- [3] J. S. Kim, R. H. Friend, and F. Cacialli, *Appl. Phys. Lett.* **74**, 3084 (1999).
- [4] S. A. Carter, M. Angelopoulos, S. Karg, P. J. Brock, and J. C. Scott, *Appl. Phys. Lett.* **70**, 2067 (1997).

- [5] J.-S. Kim, R. H. Friend, I. Grizzi, and J. H. Burroughes, *Appl. Phys. Lett.* **87**, 023506 (2005).
- [6] W. L. Yu, J. Pei, W. Huang, and A. J. Heeger, *Adv. Mater.* **12**, 828 (2000).
- [7] L. C. Palilis, D. G. Lidzey, M. Redecker, D. D. C. Bradley, M. Inbasekaran, E. Woo, and W. Wu, *Synth. Met.* **111**, 159 (2000).
- [8] L. C. Palilis, D. G. Lidzey, M. Redecker, D. D. C. Bradley, M. Inbasekaran, E. Woo, and W. Wu, *Synth. Met.* **121**, 1729 (2001).
- [9] M. Sims, D. D. C. Bradley, M. Ariu, M. Koeberg, A. Asimakis, M. Grell, and D. G. Lidzey, *Adv. Funct. Mater.* **14**, 766 (2004).
- [10] H. Riel, W. Brütting, T. Beierlein, E. Haskal, P. Müller, and W. Riess, *Synth. Met.* **111**, 303 (2000).
- [11] M. Redecker, D. D. C. Bradley, M. Inbasekaran, and E. P. Woo, *Appl. Phys. Lett.* **73** 1565 (1998).
- [12] T. Förster, *Discuss. Faraday Soc.* **27**, 7 (1959).