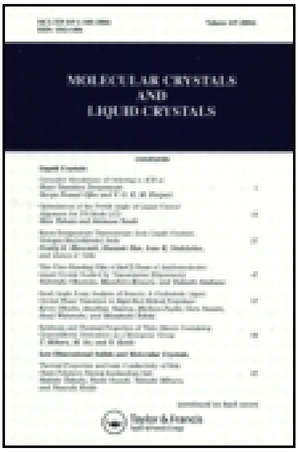

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Efficient Solution-Processed Polymer Light-Emitting Diodes Based on Poly(N-substituted-2,7-carbazole) Derivative

Sung Kwang Ahn [a], Myungkwan Song [a], Yeong-Soon Gal [b], Jae Wook Lee [c] & Sung-Ho Jin [a]

[a] Department of Chemistry Education, Interdisciplinary Program of Advanced Information and Display Materials, Institute for Plastic Information and Energy Materials, Busan, 609-735, Korea

[b] Polymer Chemistry Lab., Kyungil University, Hayang, 712-701, Korea

[c] Department of Chemistry, Dong-A University, Busan, 604-714, Korea

Version of record first published: 17 Sep 2012.

To cite this article: Sung Kwang Ahn , Myungkwan Song , Yeong-Soon Gal , Jae Wook Lee & Sung-Ho Jin (2012): Efficient Solution-Processed Polymer Light-Emitting Diodes Based on Poly(N-substituted-2,7-carbazole) Derivative, Molecular Crystals and Liquid Crystals, 567:1, 95-101

To link to this article: http://dx.doi.org/10.1080/15421406.2012.702436

Mol. Cryst. Liq. Cryst., Vol. 567: pp. 95–101, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.702436

Efficient Solution-Processed Polymer Light-Emitting Diodes Based on Poly(*N*-substituted-2,7-carbazole) Derivative

SUNG KWANG AHN,[1] MYUNGKWAN SONG,[1] YEONG-SOON GAL,[2] JAE WOOK LEE,[3] AND SUNG-HO JIN[1,*]

[1]Department of Chemistry Education, Interdisciplinary Program of Advanced Information and Display Materials, and Institute for Plastic Information and Energy Materials, Busan 609-735, Korea
[2]Polymer Chemistry Lab., Kyungil University, Hayang 712-701, Korea
[3]Department of Chemistry, Dong-A University, Busan 604-714, Korea

To investigate electroluminescent (EL) properties of a novel π-conjugated polymer, poly[N-(3,4-bis(decyloxy)phenyl)carbazolyl-2,7-vinylene)] (PCzV) was synthesized. The polymer is soluble in common organic solvents such as chloroform and chlorobenzene and could be easily spin-coated onto an indium-tin oxide coated glass substrate to obtain high quality optical thin films. The polymer has a weight-average molecular weight (M_w) of ca. 3.86×10^4 with a polydispersity of 1.60. The polymer light-emitting diodes (PLEDs) with a configuration of ITO/PEDOT:PSS/polymer/OXD-7/LiF/Al were fabricated. The maximum luminance and luminance efficiency showed 1207 cd/m^2 and 1.11 cd/A with CIE coordinate of (0.15, 0.27), respectively.

Keywords poly[N-(3; 4-bis(decyloxy)phenyl)carbazolyl-2; 7-vinylene)]; polymer light-emitting diodes; π-conjugated polymer

Introduction

The first efficient polymer light-emitting didodes (PLEDs) based on poly(*p*-phenylene-vinylene) (PPV) fabricated by Friend's group in 1990 [1]. The field of PLEDs had attracted tremendous interests from both academic and industrial laboratories especially for the development of full-color displays, which required polymers emitting three basic colors of blue, green, and red. Among these three colors, most of the blue emitting materials for PLEDs have been developed, because the pure blue emission is regarded the most primary color and is difficult to realize when π-conjugated polymers are used as the emitter [2]. π-Conjugated polymers have a several merit in that they have a high quantum yield even in a solid thin-film state, which can simplify a process of fabricating PLEDs by easy methods such as spin coating and inkjet printing. Therefore, it is believed that the next generation of flat panel displays could be made from such π-conjugated polymers. Among the various kinds of conjugated polymers, the PPVs [3], polyfluorenes [4], polythiophenes [5], and

---

[*] Address correspondence to Sung-Ho Jin, Department of Chemistry Education, Interdisciplinary Program of Advanced Information and Display Materials, and Center for Plastic Information System, Pusan National University, Busan 609-735, Korea. E-mail: shjin@pusan.ac.kr

polycarbazoles [6] are a promising class of blue-emitting materials for PLEDs because of their good processability and high fluorescent performances. In particular, polycarbazoles and derivatives have been investigated polymers for opto-electronic and electronic applications due to their excellent hole mobility and photoconductive properties [7]. In general, polycarbazoles linked at 3,6- or 2,7-positions have advantages of little formation of excimers and free of the keto-defects [8]. Specially, poly(2,7-carbazole) should allow extension of π-conjugation length through polymer main chain, which can be expected to enhance the luminescent properties. As a result, the effective π-conjugation along the polymer main chain is key parameter to explain the superior luminescent properties of poly(2,7-carbazole) derivatives. For instances, some 2,7-linked carbazole homopolymers and copolymers have been synthesized from *N*-benzoyl [9], *N*-octyl or ethylhexyl [10], and a variety of *N*-alkyl carbazoles [11]. Recently, Morin and co-workers have reported the synthesis of novel 2,7-carbazolenevinylene-based polymers and oligomers [12, 13]. In this case, the introduction of a vinylene unit provides a well-defined method for forming co-planar molecules with an elongated conjugated length, which should help to maximize the formation of molecules in thin films [14]. Also, the simple control of molecular structures could potentially possible the fine tuning of their electronic properties. Based on this design principal, we recently reported a novel π-conjugated polymers, poly(N-dialkoxyphenylcarbazolyl-2,7-vinylene) (PCzV) derivatives by using Gilch polymerization for the application of organic solar cells [15]. As the extension of our work, in this paper, we describe our strategy in improving the EL properties of PCzV, which could be useful for blue PLEDs applications.

Experimental

Materials

9-(3,4-Bis(decyloxy)phenyl)-2,7-bis(chloromethyl)carbazole was prepared according to our previously report [15]. 1,3-Bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazo-5-yl]benzene (OXD-7) and LiF were purchased from Lumtec and Aldrich Co.

Synthesis of Poly[N-(3,4-Bis(Decyloxy)Phenyl)Carbazolyl-2,7-Vinylene)] [PCzV]

A potassium tert-butoxide solution (0.92 mL of a 1.0 M solution in THF) was added dropwise by using a syringe pump over a 15 min period to a 0°C solution of 9-(3,4-bis(decyloxy)phenyl)-2,7-bis(chloromethyl)carbazole (10) (100 mg, 0.15 mmol) in freshly distilled THF (12 mL) under N_2 atmosphere. The solution was stirred at 0°C for 50 min and cooled. End capping was performed by the addition of 3–4 drops of 4-tert-butylbenzyl bromide followed by stirring for 15 min at room temperature. The solution was poured into methanol and the precipitate was removed by filtration. After carrying out successive Soxhlet extractions, the polymer was obtained by pouring the solution into methanol. The resulting polymer, PCzV (49 mg, 55%) was obtained by drying under reduced pressure.

The molecular weight and polydispersity of the polymer were determined by using gel permeation chromatography (GPC) using a PLgel 5 μm MIXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent and calibration with polystyrene standards. PCzV. ^{1}H NMR ($CDCl_3$, δ ppm): 8.12–7.94 (br, 2H, aromatic protons), 7.57–7.36 (br, 4H, aromatic protons), 7.18–6.79 (br, 5H, aromatic and vinylic protons), 4.23–3.48 (br, 4H, α-protons of decyloxy position), 1.95–0.68 (br, 38H, aliphatic protons). Anal. Calcd. for PCzV: C, 82.85; H, 9.21; N, 2.42. Found: C, 77.96; H, 9.12; N, 2.22.

Fabrication and Measurement of PLEDs

The PLEDs in this work were fabricated on indium tin oxide (ITO) covered glass substrates. The substrates were ultrasonically cleaned with detergent, deionized water, acetone, and isopropyl alcohol. Poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS) (CLEVIOS P VP AI 4083) was spin-coated onto the pre-cleaned patterned ITO glasses, yielding a layer with a thickness of 30 nm. The PEDOT:PSS layer was then baked at 150°C for 20min. The polymer films were prepared through spin-casting of polymer solution in concentration of 0.5 wt% in chlorobenzene. The polymer solution was used in the device fabrication were filtered with 0.20 μm PTFE syringe filter. The emitting layer was then annealed at 80°C for 30 min. A typical cathode consists of OXD-7/LiF/Al deposited at a pressure of 5×10^{-6} Torr. The film thickness was measured with an α-Step IQ surface profiler (KLA Tencor, San Jose, CA). OXD-7(20 nm), LiF (1 nm), and Al (100 nm) were deposited, yielding an effective area, 4 mm^2. To characterize the PLEDs, the current density-voltage-luminescence (*J*-*V*-*L*) changes were measured using a current/voltage source meter (Keithley 236) and an optical power meter (CS-1000). All processes and measurements mentioned above were carried out in the open air at room temperature.

Results and Discussion

Figure 1 shows the relative HOMO and LUMO energy levels of the materials used to fabrication for PLEDs. The HOMO (−5.29 eV) and LUMO (−2.79 eV) energy levels of PCzV was determined by using cyclic voltammerty. The energy level diagram shows that the HOMO and LUMO energy levels of PCzV are well aligned to the HOMO energy level of PEDOT:PSS and LUMO energy level of OXD-7, respectively. Holes and electrons

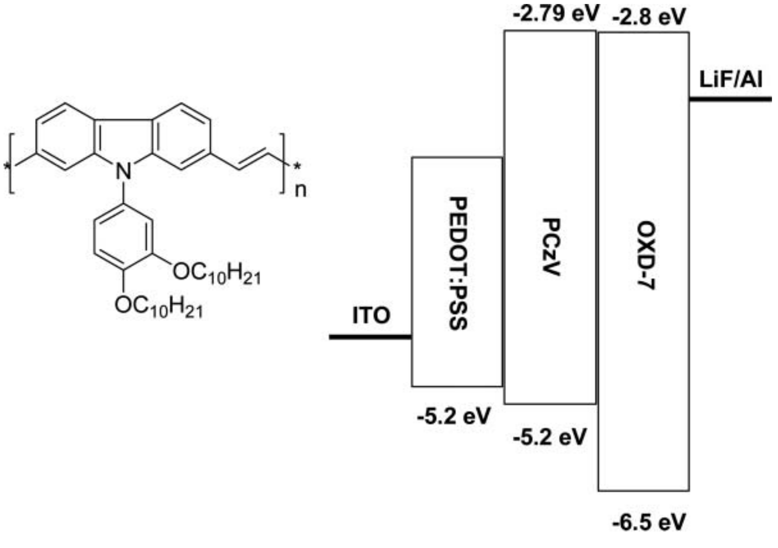

Figure 1. Molecular structure of PCzV and energy levels of the materials used in this study.

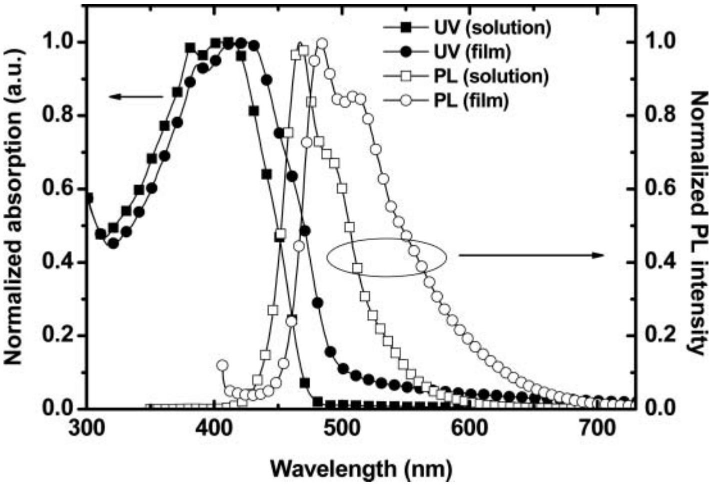

Figure 2. Normalized UV-visible and PL spectra of PCzV in solution and film states.

are directly transferred by PEDOT:PSS and OXD-7, due to the negligible HOMO and LUMO energy gap of 0.09 and 0.01 eV between PEDOT:PSS and OXD-7. Moreover, the introduction of OXD-7 layer was used both as a hole blocking layer and electron transporting layer with exciton blocking function.

Figure 2 shows the normalized UV-visible and PL spectra of the PCzV in dilute chloroform solution and film state. The absorption spectra of the PCzV contain two broad peaks at 381 nm and 403 nm in solution state and at 386 nm and 417 nm in film state. These characteristics vibronic features can be attributed to the π-π^* transitions of the carbazole segment. The energy band gaps (E_g) of the PCzV estimated from the absorption edge of the film state is 2.50 eV. The PL spectrum of PCzV has maxima at 467 nm and shoulder at 492 nm in solution state and at 482 nm and 510 nm in film state. The PL peaks observed

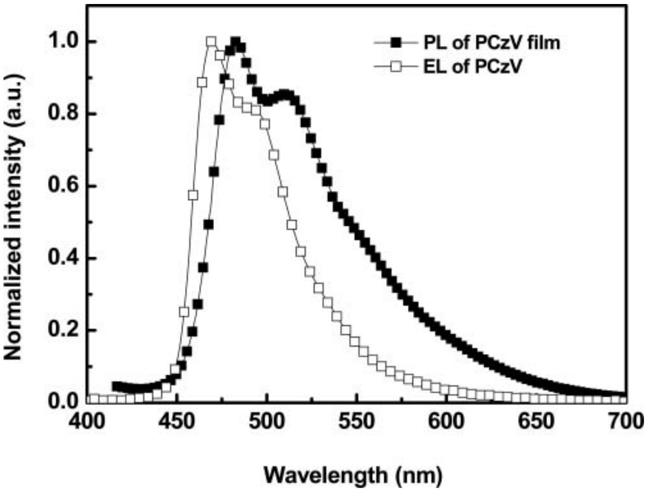

Figure 3. EL and PL spectra of PCzV.

Table 1. PLED performance of PCzV

Compound	Turn-on (V)[a]	L_{max} (cd/m^2)	LE_{max} (cd/A)	PE_{max} (lm/W)	CIE(x,y)[b]
PCzV	4.2	1207	1.11	0.39	0.15, 0.27

[a] luminance is 1 cd/m^2.
[b] Recorded at 30 mA/cm^2.

around 450 nm in chloroform solution and 470 nm in the film state are attributed to the 0–0 emission. The other PL peaks that appear in the region of longer wavelength are mainly attributable to vibronic effects in solution state and combined vibronic and excimeric effects in the film state. The vibronic fine structure is generally related with a rigid matrix and well

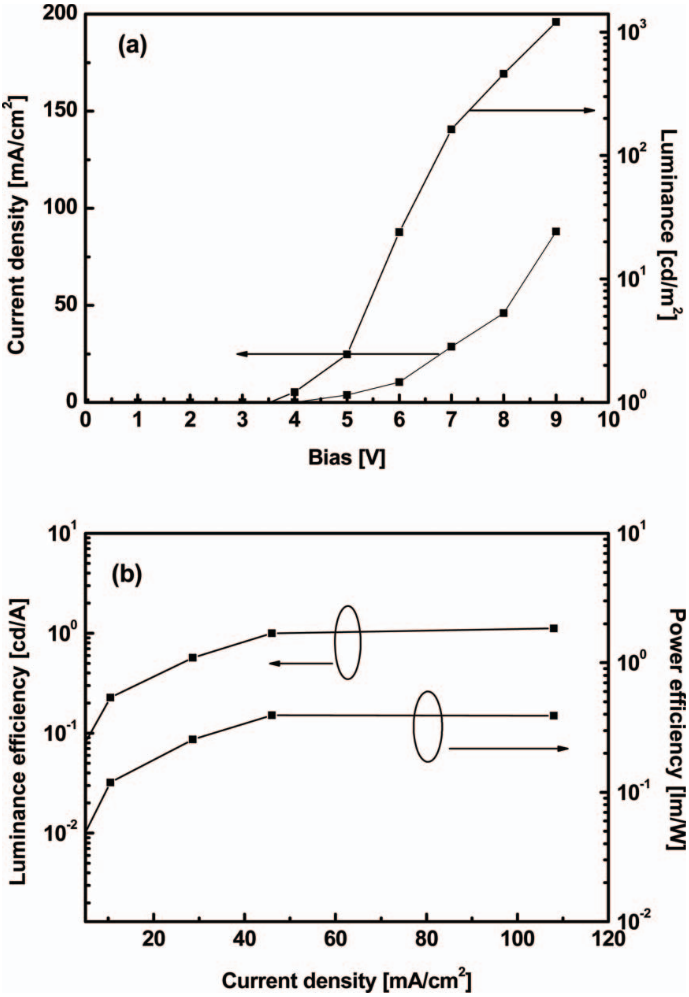

Figure 4. (a) Current density-voltage-luminance (*J-V-L*) and (b) current efficiency and power efficiency-current density characteristics of PCzV.

defined polymer backbone in the excited state [16]. The PL quantum yield in chloroform solution when excited 365 nm 0.10, measured relative to 9,10-diphenylanthrancene ($\Phi_f =$ 0.9) as a standard [17].

To investigate the EL properteis of PCzV, we fabricated PLED with a configuration of ITO/PEDOT:PSS (40 nm)/EML (80 nm)/OXD-7 (20 nm)/LiF (1nm)/Al (100 nm). Figure 3 shows the EL spectrum of the PCzV-based PLED at a current density 30 mA/cm^2 and PL spectra of films. The PLEDs exhibit sky-blue emission with peak maxima at 469 nm and CIE coordinates of (0.15, 0.27). As compared to the PL spectra of the PCzV film, the EL spectra show a little maximum peak wavelength and the shape of the spectra. It is well-known that the EL spectra of PLEDs are generally dependent on the driving voltage because of the shift of emission zone. It is mainly attributed to the difference in charge carrier mobility in the organic layer under the same electric field. The PLEDs performances are summarized in Table 1.

Figure 4 (a) shows the current density-voltage-luminance (*J-V-L*) characteristics of the PLED. The maximum luminance of the PLEDs using PCzV exhibited 1207 cd/m^2 and its turn-on voltages was 4.2 V. The low turn-on voltage and high current density were attributed to the efficient hole or electron injection from EML to PEDOT:PSS and ETL due to the negligible energy barrier. However, the poor luminance of the PLEDs based on PCzV could be explained as being partly due to the very low fluorescence quantum yields. Although the solid-state PL quantum yields were not calculated, we note that PCzV had the highest PL quantum yield ($\Phi_f = 0.10$) in solution state.

Figure 4 (b) shows the current efficiency and power efficiency versus the current density characteristics of the PLED. The maximum current and power efficiency of the PLEDs using PCzV found to be 1.11 cd/A and 0.39 lm/W, respectively.

Conclusions

In summary, a novel π-conjugated polymer, PCzV-based PLEDs with the configuration of ITO/PEDOT:PSS/polymer/OXD-7/LiF/Al were fabricated. The PLEDs exhibited a maximum luminance, current and power efficiency values of 1207 cd/m^2, 1.11 cd/A and 0.39 lm/W, respectively. The PLEDs as the sky-blue emissive layer shows a stable color purity of (0.15, 0.27) over a wide range of driving voltages.

Acknowledgment

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) grant funded from the Ministry of Education, Science and Technology (MEST) of Korea for the Center for Next Generation Dye-sensitized Solar Cells (No. 2011-0001055) and two years by Pusan National University Grant.

References

[1] Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burns, P. L., & Holmes, A. B. (1990). *Nature (London)*, *347*, 539.

[2] Avilov, B. I., Marsal, P., Bre′das, J.-L., & Beljonne, D. (2004). *Adv. Mater.*, *16*, 1624.

[3] Roviello, A., Borbone, F., Carella, A., Diana, R., Roviello, G., Panunzi, B., Ambrosio, A., & Maddalena, P. J. (2009). *Polym. Sci., Part A: Polym. Chem.*, *47*, 2677.

[4] Inagi, S., Hayashi, S., & Fuchigami, T. (2009). *Chem. Commun.*, 1718.

[5] Zou, L., Fu, Y., Yan, X., Chen, X., & Qin, J. J. (2008). *Polym. Sci., Part A: Polym. Chem.*, *46*,702.

[6] Grazulevicius, J. V., Strohriegl, P., Peilichowski, J., & Pielichowski, K. (2003). *Prog. Polym. Sci.*, *28*, 1297.

[7] Blouin, N., & Leclerc, M. (2008). *Acc. Chem. Res.*, *41*, 1110.

[8] Morin, J.-F., Leclerc, M., Ade′s, D., & Siove, A. (2005). *Macromol. Rapid. Commun.*, *26*, 761.

[9] Zotti, G., Schiavon, G., Zecchin, S., Morin, J.-F., & Leclerc, M. (2002). *Macromolecules*, *35*, 2122.

[10] Pan, X., Liu, S., Chan, H. S. O., & Ng, S. C. (2005). *Macromolecules*, *38*, 7629.

[11] Iraqi, A., & Wataru, I. (2004). *Chem. Mater.*, *16*, 442.

[12] Morin, J. F., Drolet, N., Tao, Y., & Leclerc, M. (2004). *Chem. Mater.*, *16*, 4619.

[13] Drolet, N., Morin, J. F., Leclerc, N., Wakim, S., Tao, Y., & Leclerc, M. (2005). *Adv.Funct. Mater.*, *15*, 1671.

[14] Winder, A., Winder, J., & Winder, Y. J. (2002). *Phys. Chem. A*, *109*, 7197.

[15] Song, M., Park, J. S., Yoon, K. J., Kim, C. H., Im, M. J., Kim, J. S., Gal, Y. S., Lee, J. W., Lee, J. H., & Jin, S. H. (2010). *Org. Electron.*, *11*, 969.

[16] Cimrova, V., Remmers, M., Neher, D., & Wegner, G. (1996). *Adv. Mater.*, *8*, 146.

[17] Eaton, D. F. (1988). *pure. Appl. Chem.*, *60*, 1007.