Red Electrophosphorescence from Poly(BP-*alt*-BCV) Conjugated Polymer Doped with an Ir-Complex

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Abstract

A new blue electroluminescent conjugated polymer, poly(BP-alt-BCV), was prepared by Hornor-Emmons polycondensation and used as a host polymer for the phosphorescent dopant, $(bsn)_2Ir(acac)$. Poly(N-vinylcarbazole) (PVK), known as a blue EL material, was also used for comparison with poly(BP-alt-BCV). Electrophosphorescence of PLEDs with these dopant/host systems was investigated in terms of luminescence, efficiency, emission color, and energy transfer.

1. Introduction

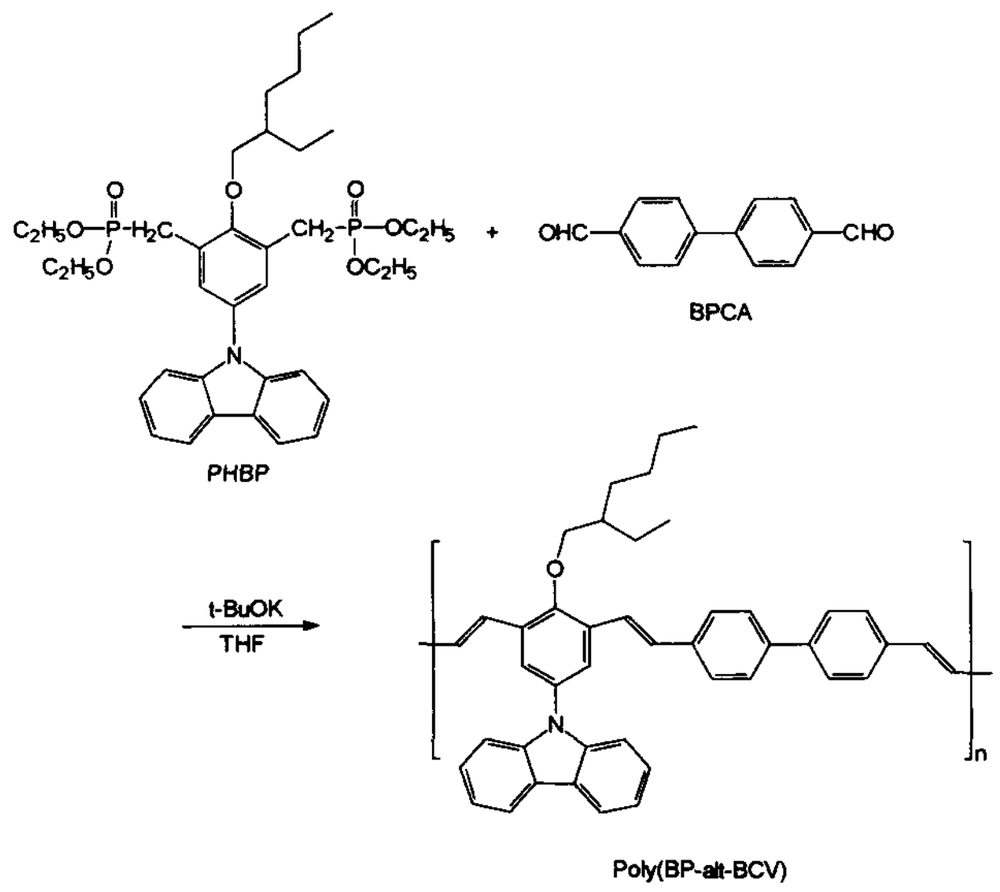
Conjugated polymers recently have found an important application in the field of organic light-emitting diode(OLED) devices. Conjugated polymers are especially useful in polymer LEDs (PLEDs) since they could readily incorporated in OLED devices by simple spin-coating method. Because of these advantages it is envisaged that PLEDs may provide the platform for the next generation of displays [1,2]. However, recent research in OLEDs has focused on the synthesis and evaluation of new phosphorescent materials in an effort to improve EL efficiencies [3]. These phosphorescent materials, especially consisting of iridium complexes with pyridine derivatives as ligand, have been utilized as dopants both in the OLEDs and PLEDs for the purpose of improving quantum efficiency and color tuning .

In this work, a new blue emitting poly (BP-*alt*-BCV) conjugated polymer containing a carbazole moiety as a pendent group in the repeating unit was synthesized by using Horner-Emmons polycondensation [4,5]. Single and double layer PLEDs using poly(BP-*alt*-BCV) as a host and $(bsn)_2Ir(acac)$ as a dopant in the emissive layer were fabricated and evaluated in terms of luminance, efficiency, emission color, and energy transfer.

2. Experimental

2.1. Synthesis

As presented in Scheme 1, poly(BP-*alt*-BCV) was synthesized by the reaction of [5-carbazol-9-yl-3-(diethoxy-phosphorylmethyl)-2-(2-ethylhexyloxy)-benzyl]-phosphonic acid diethyl ester (PHBP) and 4,4'-biphenyldicarboxaldehyde (BPCA) both prepared in the previous synthetic steps [6]. Poly(BP-*alt*-BCV) was obtained in 52% yield. GPC: Mw = 13,080 g/mol; Mw/Mn = 1.34.



Scheme 1. Synthetic route for poly(BP-*alt*-BCV) conjugated polymer.

2.2. Characterization

^{1}H-NMR spectra were taken on a Varian Unity Plus 300. Molecular weight and molecular weight distribution were measured by Waters gel permeation chromatograph (GPC) equipped with Styragel HR 5E column using THF as eluent against polystyrene standards at room temperature. UV-visible absorption spectra were obtained by Shimadzu UV-2100. The photoluminescence (PL) spectra excited by He-Cd laser at 325 nm were monitored by Optical Multichannel Analyzer (Laser Photonics, OMA system). Electroluminescence (EL) spectra and color coordinates were measured by using Spectroscan PR 704 (Photoresearch Inc.). Current and luminance vs. voltage profiles were obtained by using a dc power supply connected with Model 8092A Digital Multimeter (Hyun Chang Product Co. Ltd) and luminance meter (Minolta LS-100) equipped with close-up lens (No. 110, Φ 40.5 mm) at room temperature, respectively.

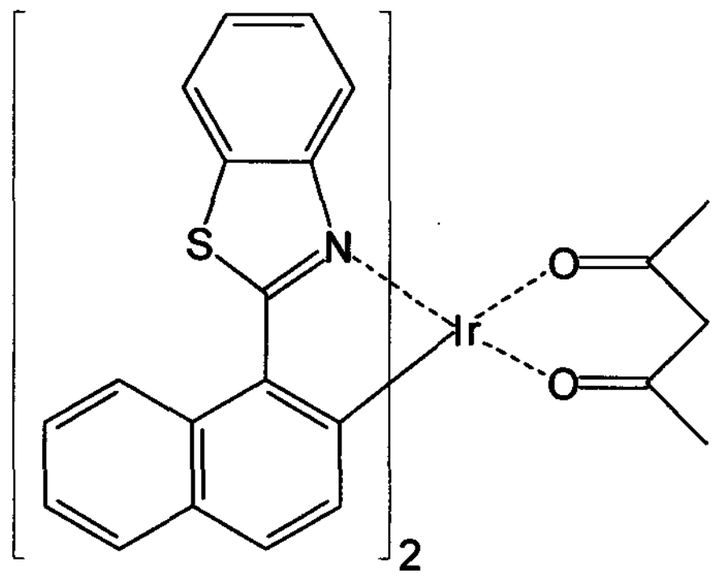
2.3. PLED Fabrication

Single layer PLEDs were made by using poly(BP-*alt*-BCV) as the emitting layer. Indium-tin oxide (ITO) coated glass was cut into 2.0 cm × 2.0 cm, and electrode area was prepared by photoetching technique. It was sequentially cleaned in an ultrasonic bath of acetone, methanol, and mixture of isopropyl alcohol and water (1:1 by vol.) solution. Solution (1 wt%) of poly(BP-*alt*-BCV) in tetrachloroethane (TCE) after filtration using MFS filter (0.45 μm pore size) was spin-coated on the ITO glass at 2500 rpm for 25 s and dried at 80 °C for 1 hr to give an emissive layer with a thickness of about 200-300 Å. Al was deposited at a rate of 20 Å/sec by thermal evaporation to give single layer [ITO/poly(BP-*alt*-BCV)/Al] PLED. In the case of double layer [ITO/poly(BP-*alt*-BCV)/Alq_3/Al] PLED, after drying the emission layer the electron transporting Alq_3 layer was deposited with thermal evaporator.

Ir-complex doped single and double layer PLEDs were also fabricated. A solution of $(bsn)_2Ir(acac)$/poly(BP-*alt*-BCV) (10/90 w/w) in TCE after filtration was spin-coated on the ITO coated glass.

3. Results and Discussion

UV-visible absorption maximum ($\lambda_{max,UV}$, π-π* transition) of poly(BP-*alt*-BCV) was measured at 340 nm. PL maximum ($\lambda_{max,PL}$) values of poly(BP-*alt*-BCV) were obtained at 406 nm and 430 nm, when excited at its own $\lambda_{max,UV}$. Single layer [ITO/poly(BP-*alt*-BCV)/Al] and double layer [ITO/poly(BP-*alt*-BCV)/Alq_3/Al] PLEDs were fabricated. The luminance-voltage and luminance-efficiency profiles of both single layer and double layer PLEDs were measured, respectively. The double layer [ITO/poly(BP-*alt*-BCV)/Alq_3/Al] PLED had a maximum luminance of about 38 cd/m^2 (12 V) and a maximum efficiency of 0.001 lm/W (9 V), higher values than those (13 cd/m^2 at 14 V and 0.0002 lm/W at 14 V) of single layer [ITO/poly(BP-*alt*-BCV)/Al] PLED. This could be explained by the introduction of Alq_3 layer, resulting in confinement of holes which were transferred relatively fast in the emitting layer, poly(BP-*alt*-BCV). From the EL spectra and color coordinate measurements, values of $\lambda_{max,EL}$ and emission colors of undoped double layer [ITO/poly(BP-*alt*-BCV)/Alq_3/Al] PLEDs were determined as 440 nm and CIE (Commission Internationalde I'Eclairage) coordinates of x = 0.1794, y = 0.1878, close to the value of standard blue color established by NTSC.



Scheme 2. Structure of the phosphorescent dopant, $(bsn)_2Ir(acac)$.

The maximum luminescence and efficiency of doped double layer [ITO/$(bsn)_2Ir(acac)$ (10%) in poly(BP-*alt*-BCV)/Alq_3/Al] PLED were respectively measured to be 82 cd/m^2 (11 V) and 0.012 lm/W (11 V), while those of PLED [ITO/$(bsn)_2Ir(acac)$ (10%) in PVK/Alq_3/Al] were observed to be 45 cd/m^2 (15 V) and 0.0015 lm/W (15 V), respectively. It was considered from above results that PLED with $(bsn)_2Ir(acac)$/poly(BP-*alt*-BCV) dopant/host system

exhibited better EL properties than that with $(bsn)_2Ir(acac)$/PVK system. The CIE coordinates were measured to be x = 0.5120, y = 0.3750 (reddish orange) for [ITO/$(bsn)_2Ir(acac)$ in poly(BP-*alt*-BCV)/Alq_3/Al] PLED and x = 0.5515, y = 0.3994 (orange) for [ITO/$(bsn)_2Ir(acac)$ in PVK/Alq_3/Al] PLED.

4. Conclusion

The fundamental study on electrophosphorescence of PLED consisting of phosphorescent $(bsn)_2Ir(acac)$ dopant/host poly(BP-*alt*-BCV) matrix as an emissive layer was carried out. It was found that doped double layer [ITO/$(bsn)_2Ir(acac)$ (10%) in poly(BP-*alt*-BCV)/Alq_3/Al] PLED exhibited better luminescence and efficiency than undoped double layer [ITO/poly(BP-*alt*-BCV)/Alq_3/Al] PLED.

5. Acknowlegements

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6. References

[1] H. S. Nalwa and L. S. Rohwer, Eds.; Handbook of Luminescence, Display Materials, and Devices, Vol.1., Organic Light-Emitting Diodes; American Scientific Publishers; California, 2003.

[2] A. J. Hudson and M. S. Weaver, In Functional Organic and Polymeric Materials; T. H. Richardson, Ed; John Wiley & Sons Ltd, Chichester, 2000, pp 365 – 394.

[3] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikow, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, **395**, 151 (1998).

[4] Y. Wei, Y. Yang and J. M. Yeh, *Chem. Mater.*, **8**, 2659 (1996).

[5] F. Wudl, S. Hoger, C. Zhang, K. Pakbaz and A. J. Heeger, *Polym. Prepr.* **34**, 197 (1993).)

[6] J. J. Baek, Y. C. Jeong, L. S. Park, Y. S. Han, Y. Kwon, *J. Nonlinear Opt. Phys. Mat.* in press.