Synthesis of a novel non-conjugated Blue emitting material Copolymer and Fabrication of mono color OLED by doping various Fluorescent Dyes

Jae-Young Cho*, Hwan-Sool Oh** , Seok-Beom Yoon***, and Myung-Koo Kang****

*,**Department of Electronic Engineering, Konkuk University, Seoul, 143-701, Korea

Tel : +82-2-450-3494 Fax : +82-2-3437-5235

*E-mail : jycho@konkuk.ac.kr **E-mail : hsoh@kkucc.konkuk.ac.kr

***Major of Optical Applied Science, Kongju National University, Kongju, 314-712, Korea

Tel : +82-41-850-6126 Fax : +82-41-850-6033 E-mail : sbyoon@kongju.ac.kr

****Department of Information Communication, Keukdong College, Eumsung, 369-703, Korea

Tel : +82-43-879-3363 Fax : +82-43-879-3361 E-mail : mkkang@kdc.ac.kr

Abstracts: The existing conjugated blue emitting material polymer which has been used for the two-wavelength method white-emission has good stability and low operating voltage as merits, but the imbalanced carrier transport has been indicated as problem area. We have introduced a novel blue emitting material having perylene moiety unit with hole transporting ability and blue emitting property and triazine moiety unit with electron transporting ability into the same host chain. We have synthesized N-[*p*-(perylen-3-yl)phenyl]methacryl amide (PPMA) monomer and [N-(2,4-diphenyl-1,3,5-triazine)phenyl methacryl amide] (DTPM) monomer having blue light-emitting unit and electron transport unit, respectively by three steps. A novel non-conjugated blue emitting material Poly[N-[*p*-(perylene-3-yl) phenyl] methacryl amide-co-N-[*p*-(4,6-diphenyl-1,3,5-triazine-2-yl]phenyl]methacryl amide] (PPPMA-co-DTPM) copolymer having electron transporting unit was synthesized by the solution polymerization of PPMA and DTPM monomers with an AIBN initiator and showed high yield of 75%. It was very soluble in common organic solvents, and the fabrication of the thin film using a spin coating method was very simple. The PPPMA exhibited a good thermal stability.

1. INTRODUCTION

In a promising bid to represent the full colors through OLEDs, researchers have focused on study methods such as the dot-matrix method with emissions separating to a red, green, and blue (RGB method) and the white emission method with color filters [1-2]. There have been many studies done on the white emission method because of the existing LCD assembly lines. It still can be used and also there is ample possibility that it can be applied for not only displays but the light sources in various ways.

There are two white emission methods. One is the 3-wavelength method that mixes the existing red, green, and blue colors. The other is the 2-wavelength method that mixes the blue and orange colors [3-7]. The 2-wavelength method is gaining strength because it shows a higher efficiency, better stability, enhanced color purity, and superior manufacturing ability more than methods that using a the red-emitting material. The 2-wavelength method has many advantages in terms of fewer color interruptions, easier color controlling, and lower manufacturing costs due to a decreased number of control factors. However, researchers urgently need to develop a substitute for the 2-wavelength method because it still uses the same blue-emitting material that the 3-wavelength method uses. The single layer white OLED which uses conjugated polymer blue emitting material used for the existing 2-wavelength method has good stability but has low operating voltage and unbalanced carrier transport.

To improve this fault of conjugated polymer, recently single layer OLED using non-conjugated polymer with both electron transport unit and hole transport unit within the same host chain has been fabricated. With this method, we dissolve both carrier transport material and emitting material in a single organic solvent at the same time and perform spin coating method. So we can make devices easier and control both carrier transport rate and luminous property so that it is possible to improve luminous efficiency and stability.

In this study, as a new type of structure of emitting layer, we will synthesize a new blue emitting material copolymer which can control carriers and luminous property by introducing both perylene moiety unit with hole transport unit and emitting unit and triazine moiety unit with electron transport unit for white-emission. And then we evaluate its characteristics of the device of mono color OLED. A newly synthesized blue emitting material copolymer can also improve enhanced carrier balancing. As a non-conjugated polymer with good stability and solubility, a successful study on this material will be an important foundation which can vary the choices of material for the white OLED and the full color OLED.

2. EXPERIMENT

We had synthesized N-[*p*-(perylen-3-yl)phenyl] methacryl amide (PPMA) monomer and [N-(2,4-diphenyl-1,3,5-triazine)phenyl methacryl amide] (DTPM) monomer having a blue light-emitting unit and electron transport unit, respectively by three steps. The scheme of synthesizing PPMA monomer and DTPM monomer were shown in fig. 1 and fig. 2, respectively. And a novel non-conjugated blue emitting material Poly[N-[*p*-(perylene-3-yl)phenyl]methacryl amide-co-N -[*p*-(4,6-diphenyl-1,3,5-triazine-2-yl]phenyl] methacryl amide] (PPPMA-co-DTPM) copolymer having electron transporting unit was synthesized by the solution polymerization of PPMA and DTPM monomers with an AIBN initiator and showed a high yield of 75 %, so that it was enhanced electron transporting ability. The scheme of synthesizing PPPMA-co-DTPM copolymer was shown in fig. 3.

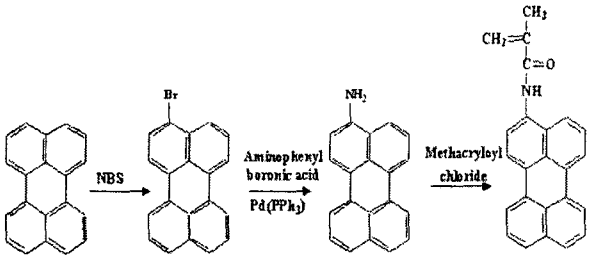

Fig. 1. The scheme of synthesizing PPMA monomer.

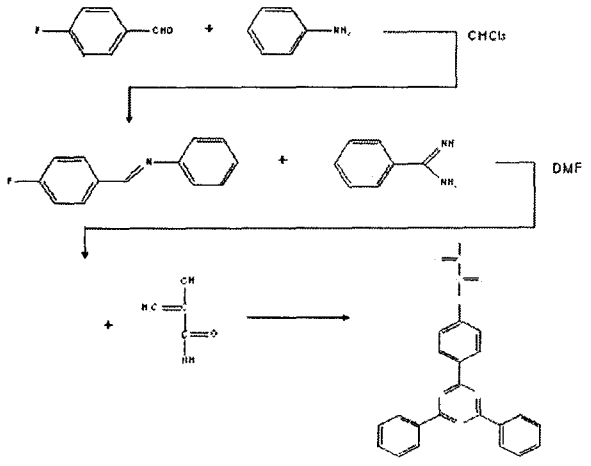

Fig. 2. The scheme of synthesizing DTPM monomer.

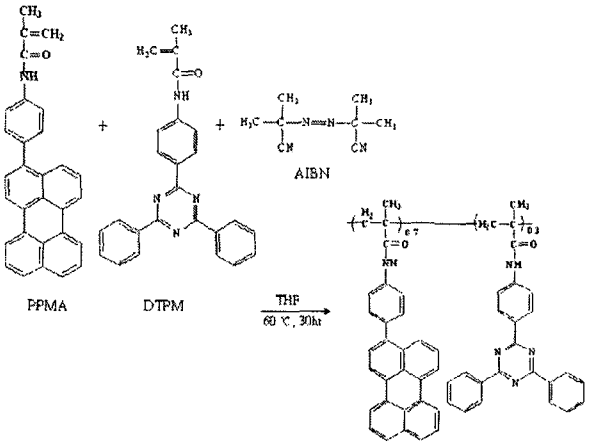

Fig. 3. The scheme of synthesizing PPPMA-co-DTPM copolymer.

We had fabricated each red, green and blue OLED using PPPMA-co-DTPM (PPPMA[70 wt%]:DTPM[30 wt%]) copolymer by doping the fluorescent dye of each red, green and blue series, then by molecular-dispersing each dye into various organic solvents for high efficiency and stabilization under various voltages.

3. RESULTS AND DISCUSSION

A novel PPPMA-co-DTPM copolymer was soluble in most organic solvents such as monochlorobenzene, tetrahydrofuran (THF), chloroform and benzene, and it was easy to configure the thin film by spin coating method. The PL peak wavelength of PPPMA-co-DTPM copolymer was 460 nm in THF solvent. The single layered device consisting of ITO/PPPMA-co-DTPM (500)/Al emitted blue light corresponding to the perylene moiety. The EL peak wavelength of PPPMA-co-DTPM copolymer appeared at 490 nm. Figure 4 shows the normalized EL spectra when the weight ratio of copolymer varied.

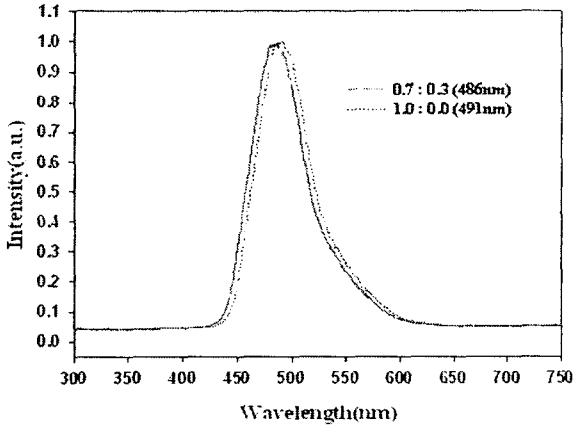

Fig. 4. Normalized EL spectra of the device using PPPMA-co-DTPM copolymer.

We had evaluated the characteristics of a mono color OLED using PPPMA-co-DTPM (PPPMA[70 wt%]:DTPM[30 wt%]) copolymer in $CHCl_3$ solvent by varying the doping concentrations of fluorescent dyes of a red, orange, green and blue series, in which a red fluorescent dye, NileRed which varied from 0.01 mol% to 1.5 mol%, an orange fluorescent dye, DCM1 which varied from 0.1 mol% to 1.0 mol%, a green fluorescent dye, C6 which varied from 0.01 mol% to 0.3 mol%, and a blue fluorescent dye, TPB, varied from 1.0 mol% to 5.5 mol%, respectively.

The basic structure of the fabricated device was glass/ITO/PPPMA[70wt%]:DTPM[30wt%]:fluorescen t dyes/Al. Table 1 shows that the conditions vary doping concentration of various fluorescent dyes.

Table 1. Doping concentrations of various fluorescent dyes.

PPPMA(70wt%):DTPM(30wt%):variable dyes conditions of spin coating ; 3000RPM, 60sec organic solvent ; 20mg/ml $CHCl_3$	
fluorescent dye	doping concentration
NileRed	0.01~1.5mol%
DCM1	0.1~1.0mol%
C6	0.01~0.3mol%
TPB	1.0~5.5mol%

Figure 5 shows EL spectra obtained at an applied voltage of 15 V when the doping concentration of a green fluorescent dye, C6, are 0.04mol% and 0.3mol% in $CHCl_3$ solvent of 20mg/ml. The EL peak emission wavelength was 513 nm and it showed to be emitted the green light.

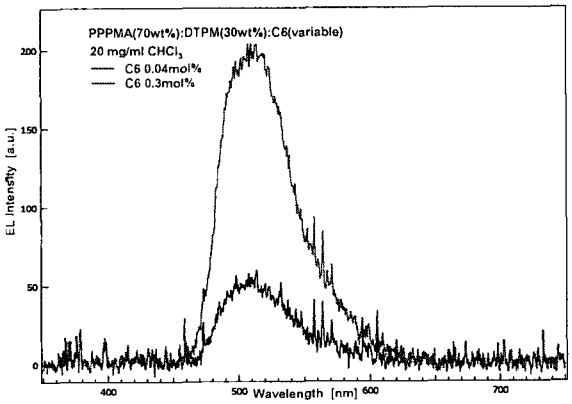

Fig. 5. EL spectra of devices for the doping concentration of C6 in 20mg/ml $CHCl_3$ solvent.

Figure 6 shows EL spectra obtained at an applied voltage of 15 V when the doping concentration of a red fluorescent dye, DCM1, are 0.1mol% and 1.0mol% in the same solvent condition. The EL peak emission wavelength was 563 nm and it showed to be emitted the orange light.

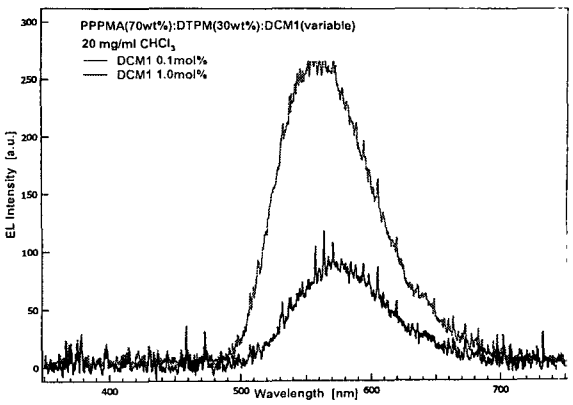

Fig. 6. EL spectra of devices for the doping concentration of DCM1 in 20mg/ml $CHCl_3$ solvent.

Figure 7 shows EL spectra obtained at an applied voltage of 15 V when the doping concentration of the red fluorescent dye, NileRed which varied from 0.1mol% to 0.3mol% to 1.0mol% to 1.2mol%. The EL peak emission wavelength was 588 nm, it showed to be emitted the orange light shifted to long-wavelength than that of the DCM1.

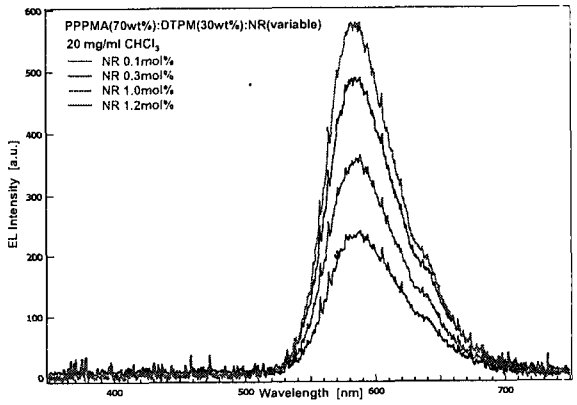

Fig. 7. EL spectra of devices for the doping concentration of NileRed in 20mg/ml $CHCl_3$ solvent.

Figure 8 shows EL spectra obtained at an applied voltage of 15 V when the doping concentrations of each fluorescent dye were NileRed of 1.2mol%, C6 of 0.04mol%, DCM1 of 0.1mol% and TPB of 5.3mol%, respectively. The EL intensity was similar to each other, except in TPB.

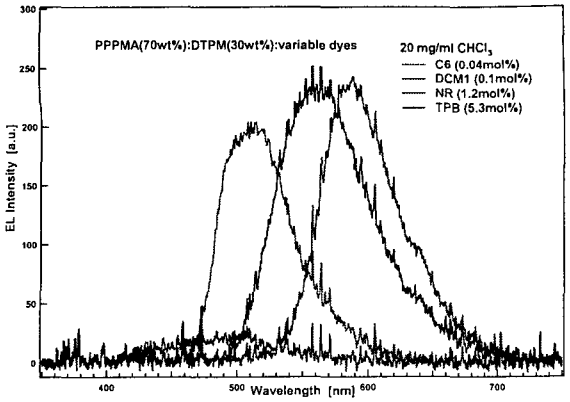

Fig. 8. EL spectra of devices for the doping concentration of each fluorescent dye in 20mg/ml $CHCl_3$ solvent.

Figure 9 shows the fluctuations of the CIE coordinates when the doping concentration of a green fluorescent dye C6 varies from 0.01 mol% to 0.02 mol% to 0.03 mol% to 0.04 mol% to 0.05 mol%. The best color purity was (0.2048, 0.5102) of CIE coordinate in case of 0.04 mol% C6, and it showed to be emitted pure green light.

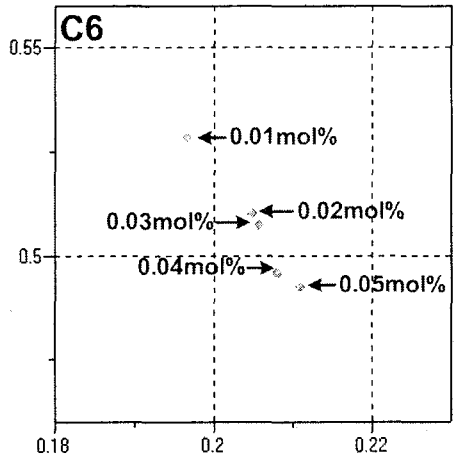

Fig. 9. CIE coordinates of the green OLED with changes in the doping concentration of C6.

Figure 10 shows the fluctuations of the CIE coordinates when the doping concentration of a red fluorescent dye NileRed varies from 0.01 mol% to 0.015 mol% to 0.02 mol% to 0.025 mol% to 0.03 mol%. The best color purity was (0.562, 0.433) of CIE coordinate in case of 0.025 mol% NileRed, but the color purity was decreased over the doping concentration of 0.025 mol%.

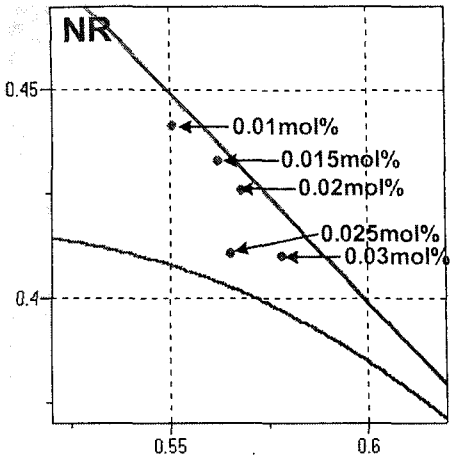

Fig. 10. CIE coordinates of the red OLED with changes in the doping concentration of NileRed.

Figure 11 shows the fluctuations of the CIE coordinates when the doping concentration of a blue fluorescent dye TPB varies from 1 mol% to 2 mol% to 3 mol% to 4 mol% to 5 mol%. As the doping concentration was increased, the EL peak emission wavelength shifted to long-wavelength. The best color purity was (0.167, 0.170) of CIE coordinate in case of 3 mol% TPB, and it showed to be emitted pure blue light.

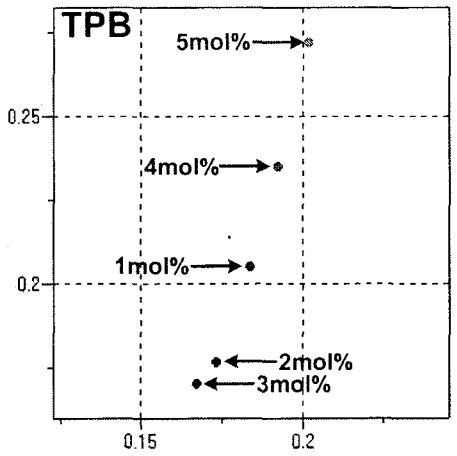

Fig. 11. CIE coordinates of the blue OLED with changes in the doping concentration of TPB.

Finally, we evaluated the electrical and optical properties of a red, green, and blue OLED. As a result, the turn-on voltage of devices was about 1.5 V, the light-emitting turn-on voltage was about 3 V, and the external quantum efficiency of devices was more than 0.5% for all injection currents. It was thought that the internal quantum efficiency was improved because of the improved carrier balancing.

4. CONCLUSION

We had synthesized N-[*p*-(perylen-3-yl)phenyl] methacryl amide (PPMA) monomer and [N-(2,4-diphenyl-1,3,5-triazine) phenyl methacryl amide] (DTPM) monomer having blue light-emitting unit and electron transport unit, respectively by three steps. A novel non-conjugated blue emitting material Poly[N-[*p*-(perylene-3-yl) phenyl] methacryl amide-co-N-[*p*-(4,6-diphenyl-1,3,5-triazine-2-yl]phenyl] methacryl amide] (PPPMA-co-DTPM) copolymer was synthesized by the solution polymerization of PPMA and DTPM monomers with an AIBN initiator for representing the white emission for a 2-wavelength method. It was very soluble in common organic solvents, and the fabrication of thin film using a spin coating method was very simple. The PL peak wavelength of PPPMA-co-DTPM copolymer was 460 nm in THF solvent. The single layered device consisting of ITO/PPPMA-co-DTPM (500 □)/Al emitted blue light corresponding to the perylene moiety. The EL peak wavelength of PPPMA-co-DTPM copolymer appeared at 490 nm.

We had evaluated the characteristics of a mono color OLED using PPPMA-co-DTPM (PPPMA[70 wt%]:DTPM[30 wt%]) copolymer in $CHCl_3$ solvent by varying the doping concentrations of fluorescent dyes of a red, orange, green and blue series, in which the C6 varied from 0.01 mol% to 0.3 mol%, the NileRed varied from 0.01 mol% to 1.5 mol% and the TPB varied from 1.0 mol% to 5.5 mol%, respectively. The EL peak wavelength of the green OLED was 513 nm at a voltage of 15 V and the CIE coordinate was (0.2048, 0.5102) in case of 0.04 mol% C6, those of the red OLED were 588 nm, the coordinate of (0.562, 0.433) in case of 0.015 mol% NileRed and those of the blue OLED were 490 nm, the coordinate of (0.167, 0.170) in case of 3 mol% TPB at the same applied voltage. The turn-on voltage of devices was about 1.5 V, the light-emitting turn-on voltage was about 3 V, and the external quantum efficiency of devices was more than 0.5% for all injection currents.

From the above results, it was believed that a newly synthesized non-conjugated blue emitting material PPPMA-co-DTPM copolymer could be applied to the white emission for a 2-wavelength method.

Acknowledgment

This work was supported by grant No. R01-2003-000-10493-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

References

[1] H. Mattoussi, H. Murata, C. D. Merritt, Y. Lizumi, J. Kido, and Z. H. Kafafi, "Photoluminescence quantum yield of pure and molecularly doped organic solid films", J. Appl. Phys. vol. 86, no 5, pp. 2642-2650, 1999.

[2] Z. L. Zhang, X. Y. Jiang, and S. H. Xu, "Energy transfer and white emitting organic thin film electroluminescence", Thin Solid Films, vol. 363, no. 1, pp. 61-63, 2000.

[3] Jing Feng, Feng Li, Wenbao Gao, and Shiyong Liu, "White light emission from exciplex using tris-(8-hydroxyquinoline)aluminum as chromaticity-tuning layer", Appl. Phys. Lett., vol. 78, no. 25, pp. 3947-3949, 2001.

[4] C. W. Ko and Y. T. Tao, "Bright white organic light -emitting diode", Appl. Phys. Lett. vol. 79, no. 25, pp. 4234-4236, 2001.

[5] Z. L. Zhang, X. Y. Jiang, W. Q. Wen, B. X. Zhang, and S. H. Xu, "A white organic light emitting diode with improved stability", J. Phys. D: Appl. Phys., vol. 34, no. 20, pp. 3083-3087, 2001.

[6] J. Y. Cho, S. J. Choi, S. B. Yoon, and H. S. Oh, "A Study on the Luminous Properties of the White-light-emitting Organic LED with Two-wavelength using DPVBi/Alq_3:Rubrene Structure", J. of KIEEME (in Korean), vol. 16, no. 7, pp. 616-621, 2003.

[7] H. S. Oh , J. Y. Cho, S. J. Choi, M. K. Kang, and S. B. Yoon, "A Study on the Optical and Electrical us Properties of the White-light-emitting Organic LED with Two-wavelength using DPVBi/Rubrene Structure", J. of KIEEME (in Korean), vol. 17, no. 2, pp. 217-222, 2004.