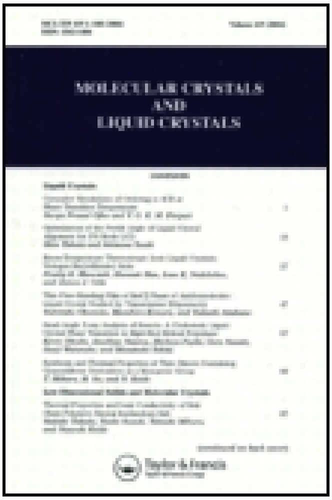

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Color Tuning of Doped PLEDs by Energy Transfer from PVK to Dopant Constituted with Biphenyl and Butadienyl Unit

Yoon Soo Han [a] , Hoyoung Kim [a] , Byeong Dae Choi [a] , Younghwan Kwon [b] , Youngjune Hur [c] , Giseop Kwak [d] , Soon Hak Kim [d] , Lee Soon Park [d] & Byeong-Dae Choi [e]

[a] Department of Nano Technology , Daegu Gyeongbuk Institute of Science & Technology , Daegu, Korea

[b] Department of Chemical Engineering , Daegu University , Gyeongsan, Gyeongbuk, Korea

[c] Advanced Display Manufacturing Research Center, Kyungpook National University , Daegu, Korea

[d] Department of Polymer Science , Kyungpook National University , Daegu, Korea

[e] DGIST , Daegu, Korea

To cite this article: Yoon Soo Han , Hoyoung Kim , Byeong Dae Choi , Younghwan Kwon , Youngjune Hur , Giseop Kwak , Soon Hak Kim , Lee Soon Park & Byeong-Dae Choi (2007) Color Tuning of Doped PLEDs by Energy Transfer from PVK to Dopant Constituted with Biphenyl and Butadienyl Unit, Molecular Crystals and Liquid Crystals, 470:1, 341-351, DOI: 10.1080/15421400701497829

To link to this article: http://dx.doi.org/10.1080/15421400701497829

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [University of Toronto Libraries] at 22:26 07 October 2014

Mol. Cryst. Liq. Cryst., Vol. 470, pp. 341–351, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701497829

Color Tuning of Doped PLEDs by Energy Transfer from PVK to Dopant Constituted with Biphenyl and Butadienyl Unit

Yoon Soo Han
Hoyoung Kim
Byeong Dae Choi
Department of Nano Technology, Daegu Gyeongbuk
Institute of Science & Technology, Daegu, Korea

Younghwan Kwon
Department of Chemical Engineering, Daegu University,
Gyeongsan, Gyeongbuk, Korea

Youngjune Hur
Advanced Display Manufacturing Research Center, Kyungpook
National University, Daegu, Korea

Giseop Kwak
Soon Hak Kim
Lee Soon Park
Department of Polymer Science, Kyungpook National University,
Daegu, Korea

Byeong-Dae Choi
DGIST, Daegu, Korea

A dopant, 4,4′-bis(dimethyl[4-(2-phenyl-buta-1,3-dienyl)phenyl]amine) biphenyl (BPAB), was synthesized, and single layered polymer light emitting diode (PLED)s, ITO/Host:Dopant/Al, were fabricated with blends of poly(vinyl carbazole) (PVK) as host and BPAB as dopant. The electroluminescence (EL) was observed in doped PLEDs. From the EL and photoluminescence (PL) spectra, the existence of energy transfer from host to dopant was verified. With increasing content of dopant (BPAB), blue emission originated from PVK reduced, but didn't

This work was supported by the DGIST Basic Research Program of the MOST, and the Regional Innovation Center (ADMRC) Program of the Ministry of Commerce, Industry, and Energy of Korea.

Address correspondence to Lee Soon Park, Department of Polymer Science, Kyungpook National University, 1370 Sankyuk-Dong, Daegu 702-701, Korea. E-mail: lspark@knu.ac.kr

completely disappear, suggesting inefficient energy transfer from PVK to BPAB. When the content of BPAB was 15 wt%, yellow green emission from PLED was observed due to partial energy transfer from PVK to BPAB.

Keywords: dopant; energy transfer; host; polymer light emitting diode (PLED)

INTRODUCTION

Semiconducting small molecules and polymers are currently the focus of industrial interest for flat panel display. Since the first report of the polymer light emitting diode s (PLEDs) from poly(*p*-phenylene vinylene) (PPV) by Cambridge group, a number of different polymers have been synthesized for use as emitting layer materials [1–4]. PLEDs have merit of large panel fabrication with low production cost by utilizing simple inkjet printing process, but the luminance and color purity are not as high as small molecular OLEDs which have adopted a doping system in emissive layer to increase luminance. As drawbacks of OLEDs using low molecular weight emitting materials, each organic layer is generally fabricated by vacuum deposition method. This method is cost ineffective, and the performance of OLEDs was greatly affected by thermal properties of organic materials and deposition conditions employed.

Recently, the efforts to enhance quantum efficiency by adopting doping system in PLEDs have been conducted by many researchers [5–8]. To understand energy transfer from host to dopant, they have chosen PVK as host material, which has wide band gap energy and good hole transporting property [9–13].

In this work, we synthesized a dopant, BPAB, containing biphenyl and butadienyl unit. Doped PLEDs were fabricated with different ratio of dopant to the host polymer, poly(vinyl carbazole), and evaluated in terms of color change and luminance efficiency.

EXPERIMENTAL

Materials

Benzyl chloride, triethylphosphite, 4-(dimethylamino)benzaldehyde, phosphoryl chloride, and potassium *tert*-butoxide were purchased from Aldrich Chemical Co., and used as received. Solvents such as N, N-dimethylformamide (DMF) and tetrahydrofurane (THF) were reagent grades and purified prior to use. Indium-tin oxide (ITO) coated glass with a sheet resistance of $30\,\Omega/\square$ was obtained from Samsung Corning Co.

Aluminum (99.99%, CERAC, USA) was used to deposit cathode electrode. Poly(vinyl carbazole) (PVK) with Mn = 48,800 and Mw/Mn = 1.68 used as a host material was purchased from Aldrich Chemical Co.

Synthesis of Dopant

The synthetic route to the dopant studied in this work is shown in Figure 1.

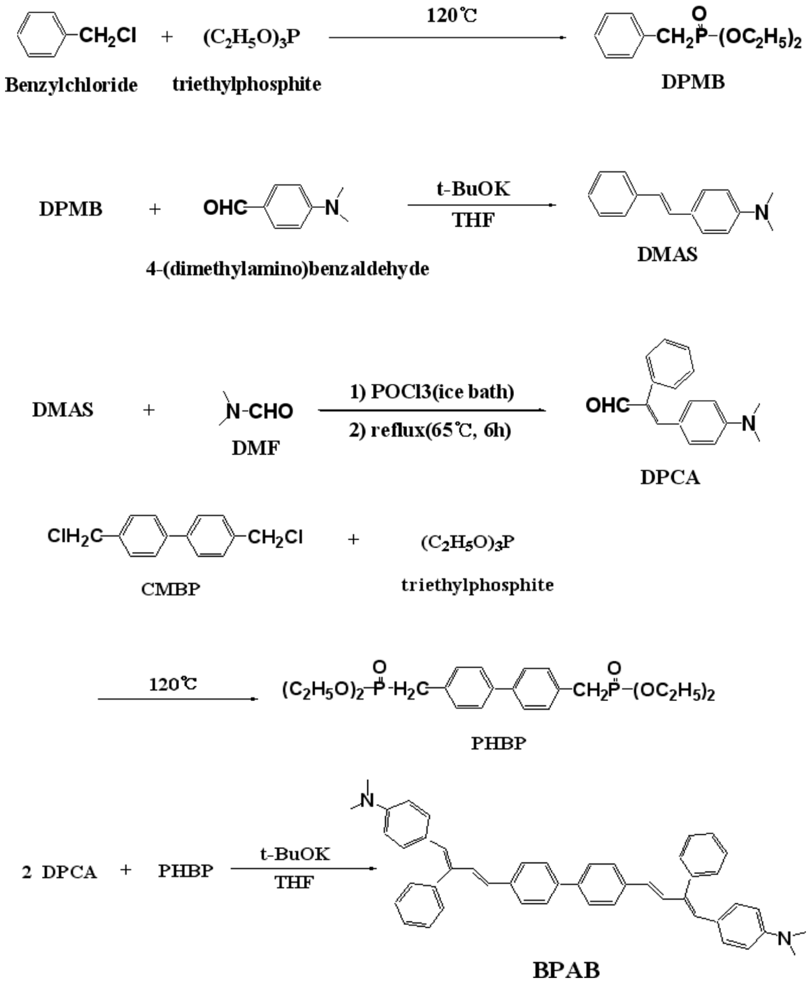

FIGURE 1 Synthetic route to dopant BPAB.

4-Dimethylaminostilbene (DMAS)

Firstly diethoxyphosphinyl methyl benzene (DPMB) was synthesized from benzyl chloride (3.7 g, 0.03 mol) and triethylphosphite (26 g, 0.17 mol) at 120°C. This reaction mixture was cooled at room temperature after stirring 14 hr, and then was stirred with 4-(dimethylamino)benzaldehyde (3 g, 0.02 mol) in the presence of t-BuOK (19 g) in THF (100 mL) for 10 hr to produce DMAS. THF and unreacted triethylphosphite were removed using vacuum, and the reaction mixture was thoroughly washed with water. The product, DMAS, was obtained by vacuum drying. Yield: 74%, ^{1}H-NMR ($CDCl_3$), δ: 7.02–7.48 (m, 9H, Ar-H), 6.75 (s, 2H, =CH−), 2.98 (s, 6H, $-CH_3$), IR (KBr), cm^{-1}: 3052 (Ar CH), 3020 (aliphatic =CH−), 2884 ($-CH_3$), 1590, 1478 (Ar C=C), 962 (trans −CH=CH−). Elemental Anal, Calcd for $C_{16}H_{17}N$: C (86.05), H (7.67), N (6.27); Found: C (86.07), H (7.94), N (6.30). Molecular weight, Calcd. for $C_{16}H_{17}N$: 223.31, Found: 223.20.

4-Dimethylamino-α-phenyl cinnamaldehyde (DPCA)

The synthesized DMAS (4.98 g, 0.022 mol) was dissolved in 40 mL of DMF and then cooled to 0°C. The 3.06 g of phosphoryl chloride solved in 10 mL of DMF was added dropwise for 10 min, and the reaction mixture was stirred at 65°C. After stirring for 6 hr, the reaction mixture was treated with 10 wt% of sodium hydroxide solution to adjust $pH = 7$. The product was precipitated. The filtered product was washed with methanol solution ($MeOH:H_2O = 50:50$ w:w). The pure DPCA was obtained by recrystallization from cyclohexane. Yield: 28.9%, ^{1}H-NMR ($CDCl_3$), δ: 9.66 (s, 1H, aldehydic hydrogen), 7.38 (d, 1H, =CH−), 7.21-7.38 (m, 9H, Ar-H), 2.97 (s, 6H, $-CH_3$), IR (KBr), cm^{-1}: 3052 (Ar CH, weak signal), 2919 ($-CH_3$), 2729 (CHO), 1656 (C=O), 1603 (C=C), 1496 (Ar C=C). Elemental Anal, Calcd. for $C_{17}H_{17}NO$: C (81.24), H (6.82), N (5.57); Found: C (81.13), H (6.91), N (5.42). Molecular weight, Calcd. for $C_{16}H_{17}N$: 251.32, Found: 251.20.

4,4′-Bis(diethoxyphosphinyl methyl)-1,1′-biphenyl (PHBP)

The procedures used for the preparation of PHBP were the same as reported [14].

4,4′-Bis(dimethyl[4-(2-pheny-buta-1,3-dienylphenyl]amine)biphenyl (BPAB)

A dopant, BPAB, was prepared by condensation reaction of DPCA and PHBP. The DPCA (1 g, 0.004 mol) and PHBP (0.78 g, 0.002 mol) were dissolved in THF, and then potassium *tert*-butoxide (1.5 g) was added. After stirring at room temperature for 12 hr, THF was removed under reduced pressure. The pure product was obtained by successive washing with water and hot methanol, followed by filtration. Yield: 88%, ^{1}H-NMR ($CDCl_3$), δ: 7.52, 7.36 (m, 8H, Ar H), 4.04 (m, 8H, $P{-}OCH_2{-}$), 3.20 (d, 4H, $Ar{-}CH_2{-}P$), 1.27 (t, 12H, $-CH_3$), IR (KBr), cm^{-1}: 3030 (Ar CH), 2987 (aliphatic CH), 1238 (P=O).

Fabrication of PLEDs

Doped single layer PLEDs were fabricated using PVK as host and BPAB as dopant. For comparison undoped single layer PLED was also fabricated. Indium-tin oxide (ITO) coated glass with a sheet resistance of $30\,\Omega/\square$ was cut into $2.0 \times 2.0\,cm^2$, and electrode area was prepared by photoetching technique. It was sequentially cleaned with acetone, methanol, and mixture of isopropyl alcohol and water (1:1 by vol.) in an ultrasonic bath. A solution of PVK:BPAB in tetrachloroethane (TCE) after filtration using MFS filter (0.45 µm pore size) was spin-coated on the ultrasonically cleaned ITO glass at 2800 rpm for 25 s and dried at 80°C for 1 hr to give an emissive layer with a thickness of about 600–800 Å. After drying the emission layer Al electrode was deposited at a rate of 20 Å/sec by thermal evaporation to give single layer [ITO/PVK:BPAB (100:0 $\sim$ 85:15 w:w)/Al] PLED. The area of deposited Mg was approximately $0.4\,cm^2$.

Measurements

The ^{1}H-NMR and FT-IR spectra of synthesized dopant were taken on a Varian Unity Plus 300 and Jasco FT/IR-620 spectrometer, respectively. UV-visible absorption spectrum of synthesized BPAB was obtained by Shimadzu UV-2100. PL spectra were obtained by optical multichannel analyzer (OMA system, laser photonics, USA). Excitation source was He-Cd laser. EL spectra were recorded by Spectroscan PR 704 (Photo-research Inc.) at 2 nm resolution and color coordinates were determined by the same instrument. Current and luminance vs. voltage profiles were obtained by using a dc power supply connected with Model 8092 A 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.

RESULTS AND DISCUSSION

Synthesis and Characterization of Dopant

The dopant, BPAB, was synthesized to investigate energy transfer from blue emitting PVK to yellow green emitting BPAB. As presented in experimental section, all the intermediates to synthesize

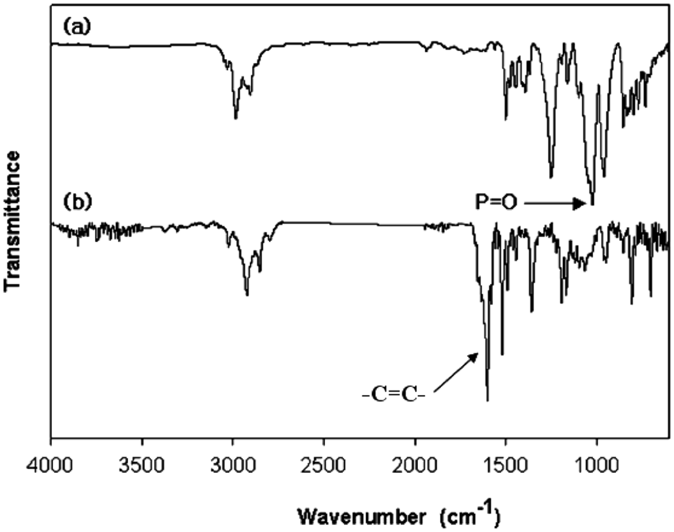

FIGURE 2 FT-IR spectra of (a) PHBP and (b) BPAB.

BPAB were characterized with ^{1}H-NMR and FT-IR. As shown in Figure 2, FT-IR spectra of PHBP and BPAB, the absorption peak ($\sim$1200 cm^{-1}) of P=O stretching mode in PHBP disappeared after Honer-Emmons condensation, and the C=C stretching mode ($\sim$1600 cm^{-1}) appeared in FT-IR spectrum of BPAB.

Optical Properties of PVK and BPAB

Energy transfer can be achieved from the excited state of host to the ground state of dopant due to good spectral overlap between the emission of host and the absorption of the dopant.[8] In order to recognize the possibility of energy transfer from PVK to BPAB, UV-Visible absorption and PL emission spectra of PVK and BPAB were measured, as can be seen in Figure 3. The absorption maxima ($\lambda_{\mathrm{max,UV}}$) were measured to be 330 and 344 nm for PVK, and 404 nm for BPAB, respectively. PL maximum ($\lambda_{\mathrm{max,PL}}$) values of PVK and BPAB were observed at 367 and 511 nm, when excited at their own $\lambda_{\mathrm{max,UV}}$, respectively. BPAB exhibited $\lambda_{\mathrm{max,UV}}$ at 404 nm, which was overlapped to a relatively large extent with PL peaks of PVK. BPAB showed $\lambda_{\mathrm{max,PL}}$ at 511 nm, but PL was not observed when excited at 330 nm, $\lambda_{\mathrm{max,UV}}$ of PVK.

PL spectra of PVK/BPAB mixtures, excited at 330 nm, were measured as a function of the BPAB content in mixtures (Fig.4). As the

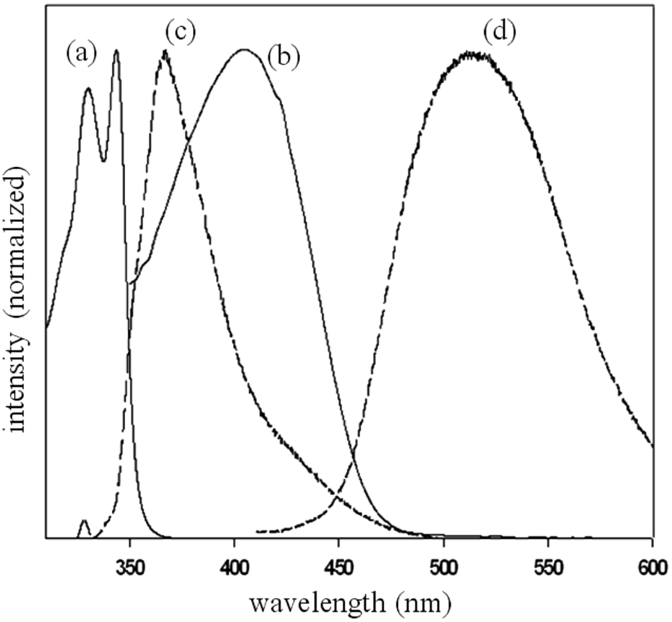

FIGURE 3 UV-visible absorption spectra of (a) PVK and (b) BPAB, and PL spectra of (c) PVK and (d) BPAB.

content of BPAB dopant was increased in the BPAB/PVK mixture solution, the PL intensity of BPAB at 511 nm steadily increased while PL intensity of PVK decreased, suggesting energy transfer between BPAB dopant and PVK host polymer.

Electro-Optical Properties of PLEDs

Figure 5 shows EL spectra of single layer PLEDs made with PVK/BPAB blend as an emitting layer. Similar to the PL spectra, PVK emission fraction decreased with increasing BPAB content. Although the emission from host PVK was reduced and emission from dopant BPAB became more dominant with increasing dopant concentration, the emission from PVK still appeared. This result suggests inefficient energy transfer from PVK to BPAB.

Color coordinates of single layer PLEDs were compared with those of standard red, green, blue, and white color established by NTSC (national television system committee) [15] in Figure 6. The emission color could be determined from these color coordinates as measured by

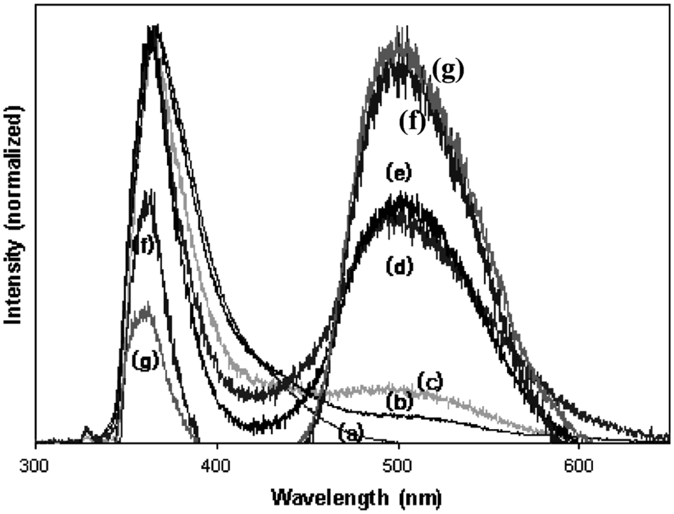

FIGURE 4 PL spectra of (a) 0, (b) 1, (c) 2, (d) 5, (e) 7, (f) 10 and (g) 15 wt% of BPAB in PVK:BPAB mixture solved in TCE. Zero wt% of BPAB means to use only PVK.

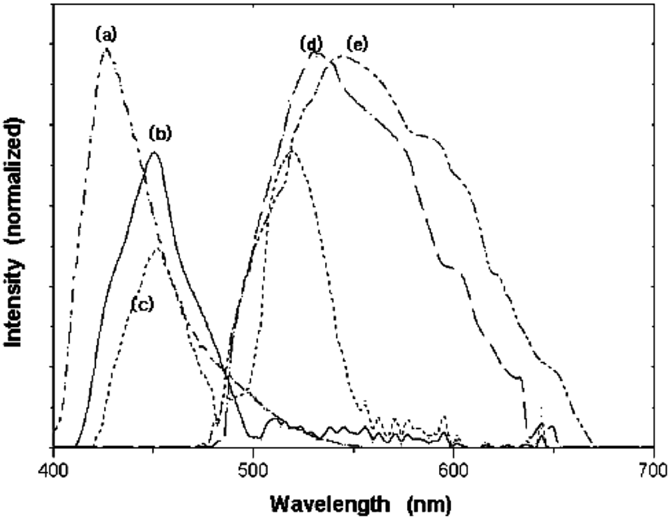

FIGURE 5 EL spectra of PLEDs made with (a) 0, (b) 1, (c) 5, (d) 10 and (e) 15 wt% of BPAB in PVK:BPAB mixture.

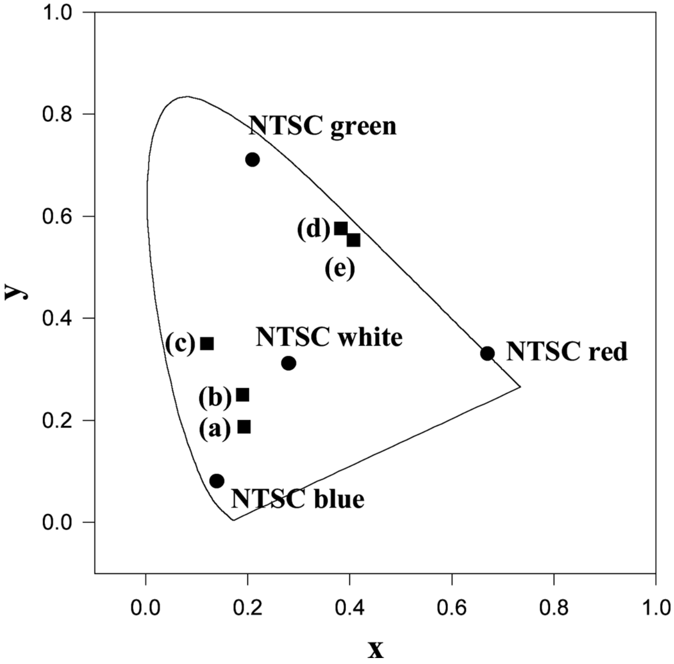

FIGURE 6 CIE 1931 chromaticity diagram showing color coordinates of PLEDs fabricated with (a) 0, (b) 1, (c) 5, (d) 10 and (e) 15 wt% of BPAB in PVK:BPAB mixture.

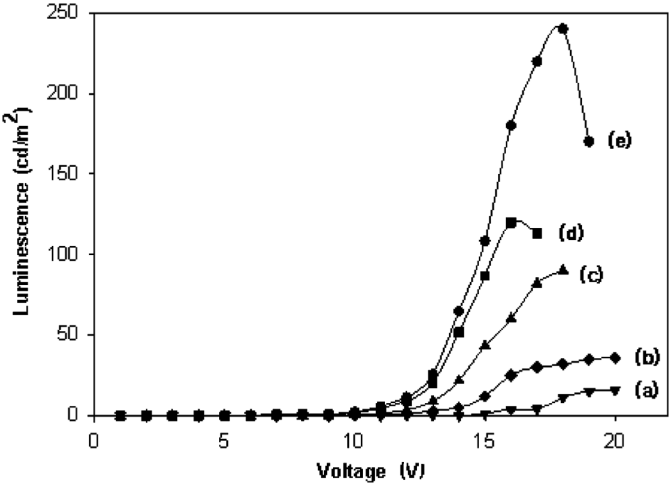

FIGURE 7 Luminance-voltage profiles of PLEDs fabricated with (a) 0, (b) 1, (c) 5, (d) 10 and (e) 15 wt% of BPAB in PVK:BPAB mixture.

Spectroscan PR-704 (Photoresearch Inc.) and Kelly's map [16] in CIE (Commission Internationale de l'Eclairage) 1931 chromaticity diagram [17]. The EL light of PVK-based PLED(ITO/PVK/Al) showed blue emission with color coordinates of x = 0.19 and y = 0.19, and the EL colors from PLEDs with 1, 5, 10 and 15 wt% of BPAB in PVK/BPAB BPAB blend were greenish blue (CIE coordinates of x = 0.19 and y = 0.25), bluish green (CIE coordinates of x = 0.12 and y = 0.35), yellow-green (CIE coordinates of x = 0.38 and y = 0.58), and yellow green (CIE coordinates of x = 0.41 and y = 0.55), respectively.

The luminance-voltage profiles are shown in Figure 7. PLED fabricated with PVK as emitting layer showed lower luminance than those of PLEDs made with PVK/BPAB blend due to energy transfer from blue emitting PVK to green emitting BPAB. The highest luminance was 240 cd/m^2 at 18 V from ITO/PVK:BPAB(85:15 w:w)/Al device.

CONCLUSIONS

Yellow green emitting dopant, BPAB, was synthesized to investigate energy transfer from host PVK and dopant BPAB in PLED. From the PL and EL studies, we could identify the existence of energy transfer, and evaluate the degree of energy transfer qualitatively. In the PVK/BPAB system, the energy transfer was observed, but incomplete. It was also found that while undoped ITO/PVK/Al device showed blue emission of high color purity, doped ITO/PVK:BPAB(85:15 w:w)/Al device exhibited yellow green emission, implying energy transfer from PVK to BPAB dopant.

REFERENCES

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

[2] Askari, S. H., Rughooputh, S. D., & Wudl, F. (1989). *Synth. Met.*, *29*, E129.

[3] Gurge, R. M., Sarker, A. M., Lahti, P. M., Hu, B., & Karasz, F. E. (1997). *Macromolecules*, *30*, 8286.

[4] Bradley, D. D. C. (1993). *Synth. Met.*, *54*, 401.

[5] Hino, Y., Kajii, H., & Ohmori, Y. (2006). *Thin Solid Films*, *499*, 359.

[6] Xu, Z., Liu, M., Chen, X., Hou, Y., Teng, F., Meng, L., & Xu, X. (2006). *Displays*, *27*, 45.

[7] Zhen, H., Jiang, C., Yang, W., Zeng, X., Zhang, C., & Cao, Y. (2005). *Synth. Met.*, *155*, 196.

[8] Wang, X., Andersson, M. R., Thomson, M. E., & Inganäs, O. (2004). *Thin Solid Films*, *468*, 226.

[9] Lee, C.-L., Lee, K. B., & Kim, J.-J. (2000). *Appl. Phys. Lett.*, *77*, 2280.

[10] Berkovich, E., Klein, J., Sheradsky, T., Silcoff, E. R., Ranjit, K. T., Willner, I., Nakhmanovich, G., Gorelik, V., & Eichen, Y. (1999). *Synth. Met.*, *107*, 85.

[11] Kwok, C. C. & Wong, M. S. (2001). *Mate. Sci. Eng. B*, *85*, 126.

[12] Duan, L., Qui, Y., He, Q., Bai, F., Wang, L., & Hong, X. (2001). *Synth. Met.*, *124*, 373.

[13] Huang, J., Zhang, H., Tian, W., Hou, J., Ma, Y., Shen, J. & Liu, S. (1997). *Synth. Met.*, *87*, 105.

[14] Han, Y. S., Kim, S. D., Park, L. S., Kim, D. U., & Kwon, Y. (2003). *J. Polym. Sci.: Part A: Polym. Chem.*, *41*, 2502.

[15] Ozawa, L. (1994). *Application of Cathodoluminescence to Display Devices*, Kodansha, Tokyo, 18–30.

[16] Agoston, G. A. (1979). Springer series in optical sciences. In: *Color Theory and Its Application in Art and Design*, MacAdam, D. L., (Ed.), Vol. 19, Springer-Verlag: Berlin, 57–59.

[17] MacAdom, D. L. (1981). Springer series in optical sciences. In: *Color Measurement; Theme and Variations*, MacAdam, D. L., (Ed.), Vol. 27, Springer-Verlag: Berlin, 17–25.