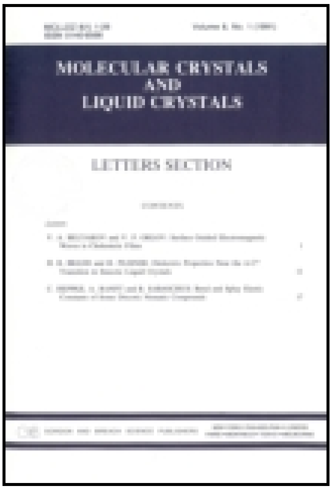
This article was downloaded by: [University Of Gujrat]
On: 11 December 2014, At: 13:42
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Synthesis of Electroluminescent Materials Based on Phosphine Oxide-Naphthoxazole Structure

Ik-Hwan Kim[a], Eunguk Kang[a], Dong-Eun Kim[b], Hoon-Kyu Shin[b] & Burm-Jong Lee[a]

[a] Department of Chemistry, Inje University, Gimhae, Korea

[b] National Center for Nanomaterials Technology, Pohang University of Science and Technology, Pohang, Korea

Published online: 17 Nov 2014.

To cite this article: Ik-Hwan Kim, Eunguk Kang, Dong-Eun Kim, Hoon-Kyu Shin & Burm-Jong Lee (2014) Synthesis of Electroluminescent Materials Based on Phosphine Oxide-Naphthoxazole Structure, Molecular Crystals and Liquid Crystals, 597:1, 88-94, DOI: 10.1080/15421406.2014.932234

To link to this article: http://dx.doi.org/10.1080/15421406.2014.932234

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

Mol. Cryst. Liq. Cryst., Vol. 597: pp. 88–94, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.932234

Synthesis of Electroluminescent Materials Based on Phosphine Oxide-Naphthoxazole Structure

IK-HWAN KIM,[1] EUNGUK KANG,[1] DONG-EUN KIM,[2]
HOON-KYU SHIN,[2] AND BURM-JONG LEE[1,*]

[1]Department of Chemistry, Inje University, Gimhae, Korea
[2]National Center for Nanomaterials Technology, Pohang University of Science and Technology, Pohang, Korea

In the course of investigation for finding new light-emitting materials based on the phosphine oxide-oxazole structure, 2-(2-(diphenylphosphoryl)phenyl)naphtho[2,3-d]oxazole (2-PPN) and 2-(4-(diphenylphosphoryl)phenyl)naphtho[2,3-d]oxazole (4-PPN) were newly synthesized. The chemical structures are characterized by ^{1}H-NMR, ^{13}C-NMR, FT-IR, UV-Vis, elemental analysis (EA), and X-ray photoelectron spectroscopy (XPS). 2-PPN and 4-PPN show a strong blue emission under excitation by UV-lamp of 365nm. The photoluminescence (PL) of 2-PPN and 4-PPN showed a blue emission in chloroform. The electroluminescence (EL) of 2-PPN and 4-PPN devices showed a green emission.

Keywords Blue emitting material; phosphine oxide-naphthoxazole; OLED; photoluminescence; electroluminescence

Introduction

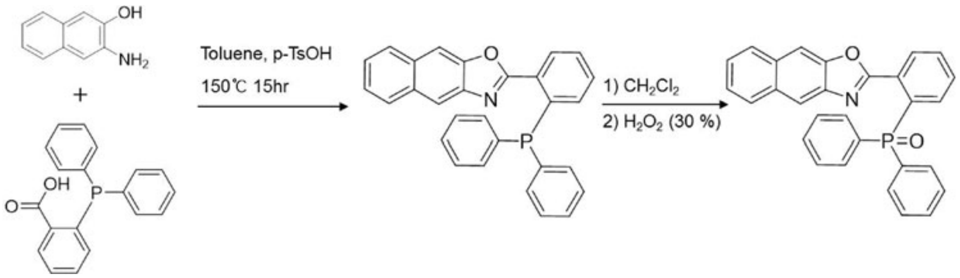
Organic light-emitting devices (OLEDs) are already progressed towards commercialization due to the advantages for full color, thin flat-panel displays and light sources. To achieve full color displays, there are three primary colors required (red, green and blue) [1–6]. Considerable efforts have been directed to the practical use of OLEDs, problems still remain for good blue emitting materials with high purity and quantum yield. Thus, a highly efficient blue OLED could be achieved if a blue emitting material having the electron trap capacity could be provided. The injected holes would be efficiently recombined with trapped electrons in such an emitting material.

An ambipolar phosphine oxide material was reported to show high power efficiency blue phosphorescent emission [7]. In this work, phosphine oxide-oxazole compounds with aromatic rings are newly synthesized, since the combination of oxygen, nitrogen, and phosphorus atoms together with naphthalene and three phenyl moieties are expected to give a blue emitting and the electron trapping properties [8]. The chemical structures of phosphine oxide-oxazole materials were elucidated by ^{1}H-NMR, ^{13}C-NMR, FT-IR, UV-Vis, EA, and XPS. Light emission properties of these materials were characterized by PL

---

[*] Address correspondence to Burm-Jong Lee, Department of Chemistry, Inje University, Gimhae 621-749, Korea; Tel.: +82-55-320-3223; Fax: +82-55-321-9718. E-mail: chemlbj@inje.ac.kr.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.



Scheme 1. Synthetic scheme of 2-PPN.

and EL spectra. Multilayered EL devices were fabricated with the synthesized materials and evaluated in terms of emission color and luminescence efficiency.

Experimental

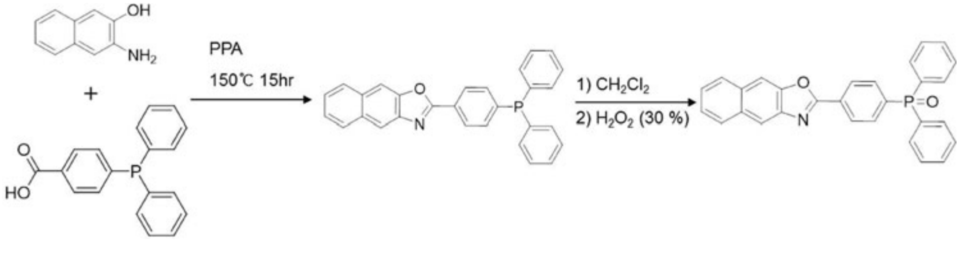
1. Materials

The reagents such as polyphosphoric acid (PPA), 3-amino-2-naphthol, 2-(diphenylphosphino)benzoic acid and 4-(diphenylphosphino)benzoic acid were purchased from Sigma-Aldrich Chemical Co. and used without further purification. p-Toluenesulfonic acid was purchased from Kanto Chemical Co. and used without further purification. Toluene was purchased from Duksan Pure Chemical Co. and used as received.

2. Synthesis

Synthetic schemes of 2-(2-(diphenylphosphoryl)phenyl)naphtho[2,3-d]oxazole (2-PPN) and 2-(4-(diphenylphosphoryl)phenyl)naphtho[2,3-d]oxazole (4-PPN) are respectively shown in Scheme 1 and 2.

2.1. Synthesis of 2-(2-(diphenylphosphoryl)phenyl)naphtho[2,3-d]oxazole (2-PPN). 3-Amino-2-naphthol (0.159 g, 1.0 mmol), 2-(diphenylphosphino)benzoic acid (0.306 g, 1.0 mmol) and p-toluene sulfonic acid (0.190 g, 1.0 mmol) were added to toluene (30 mL). The mixture was heated to 150°C for 15 hr under nitrogen. The progress of reaction was monitored by TLC. After the reaction mixture cooled, the solution was extracted with water, and the organic solution was evaporated. Then the crude intermediate in 10 mL dichloromethane were stirred in a round-bottom flask, and then H_2O_2 (1.2 mL, 10 mmol, 30%) was slowly added into the mixture while stirring at room temperature. The organic



Scheme 2. Synthetic scheme of 4-PPN.

layer was separated and washed with water. The extract was evaporated to dryness affording a pale yellow solid. The residue was dissolved in $CHCl_3$ and added to methanol in order to get solid precipitate. The crude product was purified by column chromatography with $CHCl_3$: ethyl acetate (5:1) eluent to afford pale yellow solid (0.222 g, yield 50%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.18-8.20 (m, 2H), 7.99(s, 1H), 7.86-7.93 (d, 1H), 7.78-7.82 (d, 1H), 7.72-7.76 (m, 6H), 7.59-7.63(m, 4H), 7.42-7.47(m, 1H), 7.33(s, 4H). FT-IR (cm^{-1}): 1549 (C = N), 1456, 1435 (aromatic C = C), 1190 (P = O), 1113 (C-O). EA: Calc. (%) C: 78.19, H: 4.53, N: 3.14, O: 7.18. Found (%) C: 76.56, H: 4.69, N: 1.89, O: 7.48. Found by XPS (%) C: 77.93, N: 2.95, O: 6.46, P: 8.18. XPS (eV): 131.87 (P), 284.6 (C), 398.91 (N), 530.5 (O).

2.2. Synthesis of 2-(4-(diphenylphosphoryl)phenyl)naphtho[2,3-d]oxazole (4-PPN). 3-Amino-2-naphthol (0.159 g, 1.0 mmol) and 4-(diphenylphosphino)benzoic acid (0.306 g, 1.0 mmol) were added to polyphosphoric acid (PPA) (30 mL) [9]. The mixture was heated to 150°C for 15 hr under nitrogen. The progress of reaction was followed by TLC. After the reaction mixture cooled, the reaction solution was extracted with water. The organic layer was dried by anhydrous $MgSO_4$ and filtered. Then the crude intermediate in 10 mL dichloromethane were stirred in a round-bottom flask, and then H_2O_2 (1.2 mL, 10 mmol, 30%) was slowly added into the mixture while stirring at room temperature. The organic layer was separated and washed with water. The extract was evaporated to dryness affording a pale yellow solid. The residue was dissolved in $CHCl_3$ and added to methanol in order to get solid precipitate. Crude powder was purified by column chromatography with $CHCl_3$: ethyl acetate (5:1) eluent to afford pale yellow solid (0.414 g, yield 93%).

^{1}H- NMR (500 MHz, $CDCl_3$): δ (ppm) 8.41-8.43 (q, 2H), 8.23 (s, 1H), 7.95-8.02 (q, 1H), 7.86-7.90 (m, 6H), 7.69-7.73 (q, 1H), 7.57-7.60 (m, 4H) 7.48-7.52 (m, 1H), 7.47 (m, 4H). FT-IR (cm^{-1}): 1543 (C = N), 1486, 1437 (aromatic C = C), 1179 (P = O), 1112 (C-O). EA: Calc. (%) C: 78.19, H: 4.53, N: 3.14, O: 7.18. Found (%) C: 78.18, H: 4.52, N: 2.80, O: 7.22. Found by XPS (%) C: 76.93, N: 2.85, O: 7.73 P: 8.00. XPS (eV): 131.9 (P), 284.6 (C), 398.67 (N), 533.91 (O).

3. Instrumentation

Infrared spectra were recorded on a Scimitar 1000 (Varian). ^{1}H-NMR and ^{13}C-NMR spectra were obtained with a VNMRS500 NMR spectrometer. X-ray photoelectron spectroscopy (XPS) was carried out at Busan branch of Korea Basic Science Institute. UV-Vis absorption spectra were measured by a UV-VIS Spectrometer (Shimadzu UV-3100S). The PL spectrum was measured using a Perkin-Elmer LS45 luminescence spectrometer. The characteristics of the current density-voltage-luminance (I-V-L) were measured by IVL 300 series (JBS Inc.)

4. Fabrication of OLED Device

The devices were fabricated on indium tin oxide (ITO) glass substrates. The organic layers were vacuum-deposited using thermal evaporation at a vacuum pressure of 2×10^{-7} torr. 1,4-Bis(1-naphthylphenylamino)biphenyl (NPB) as a hole transport layer, 2- or 4-PPN as an emitting layer, 1,3,5-tris(N-phenylbenzimidizol-2-yl)benzene (TPBI), 8-hydroxyquinolate aluminum (Alq_3) as electron transport layers, 8-hydroxyquinolate lithium (Liq) as an electron injection layer, and Al as a cathode were respectively employed. Each device has a following structure. 2-PPN device 1: ITO/NPB[50nm]/2-PPN[50nm]/ Liq[0.5nm]/Al[120nm],

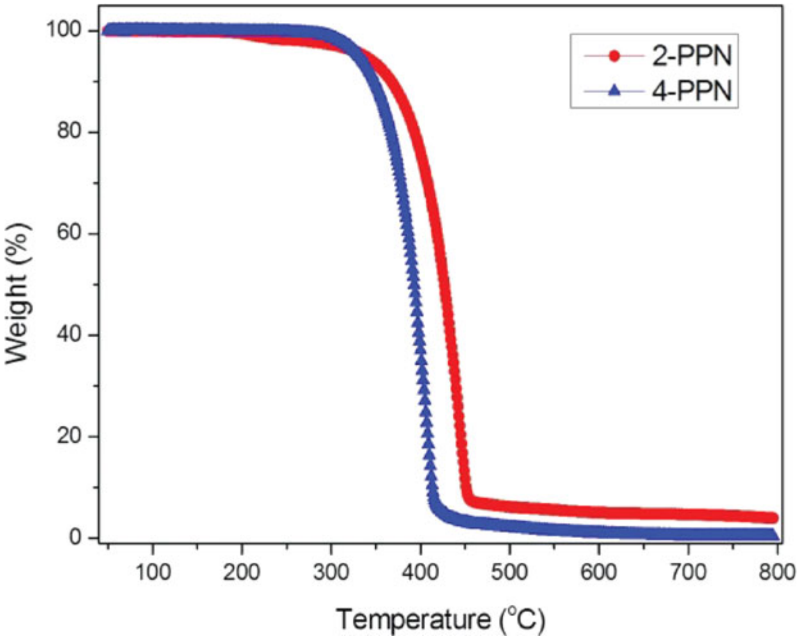


Figure 1. TGA spectra of 2-PPN and 4-PPN.

2-PPN device 2: ITO/NPB[50nm]/2-PPN[50nm] /Alq_3[15nm]/Liq[0.5nm]/Al[120nm], and 4-PPN device 1: ITO/NPB[40nm]/4-PPN[50nm]/TPBI[30nm]/Liq[0.5nm]/Al[120nm].

Results and Discussion

1. Structure Determination

When 3-amino-2-naphthol reacts with 2- or 4-(diphenylphosphino)benzoic acid, the phosphine-naphthoxazole products are first expected. However, from the spectroscopic analysis together with elemental analysis and XPS, we found that the triphenylphosphine moiety spontaneously oxidizes to triphenylphosphine oxides during synthetic procedure. We think the products are oxidized by atmospheric oxygen.

The chemical structures of 2-PPN and 4-PPN were determined by ^{1}H-NMR, ^{13}C-NMR, FT-IR, EA, and XPS. From the IR spectra of 2-PPN and 4-PPN, the disappearance of carboxyl group (1685 cm^{-1}) of 2- or 4-(diphenylphosphino)benzoic acid was observed, and the newly C=N bond (1549 cm^{-1})of oxazole ring was confirmed. ^{1}H-NMR spectra showed aromatic peaks only from 7.33 to 8.20 ppm by 2-PPN and from 7.47 to 8.43 ppm by 4-PPN. The formation of oxazole ring was also confirmed by ^{13}C-NMR spectra. The ^{13}C peaks from C atom of C=N bond were observed at 164.0 ppm by 2-PPN and at 163.8 ppm by 4-PPN. The elemental analysis and XPS spectra gave notice of oxidation of phosphine moiety to phosphine oxides. It is supposed to be oxidized by atmospheric oxygen.

2. Thermal Properties by DSC and TGA

We have measured the thermal stability and melting point of 2-PPN and 4-PPN by DSC and TGA. Figure 1 shows TGA thermograms of 2-PPN and 4-PPN. The thermal stability of OLED materials is very important, because the durability of multilayer devices significantly

Table 1. Thermal Properties of 2-PPN and 4-PPN

		TGA	
Composite	DSC T_m[a] (°C)	T_d[b] (°C)	Residue (wt%)
(a) 2-PPN	217.5	427	3.911
(b) 4-PPN	291.8	393	0.339

[a] Melting temperature determined by DSC (heat at 5°C/min and N_2 atmosphere).
[b] Decomposition temperature determined by TGA (50% weight loss at 5°C/min and N_2 atmosphere).

depends on the thermal stability of organic materials. As summarized in Table 1, 4-PPN shows higher T_m than 2-PPN, but similar degradation pattern. Both compounds reveal high thermal stability enough for OLED device.

3. *Photoluminescence (PL) Properties*

Figure 2 shows UV-Vis absorption and PL emission spectra of 2-PPN and 4-PPN in $CHCl_3$. The maximum absorption of 2-PPN and 4-PPN appeared around 266 and 276 nm, respectively, which are originated from the $\pi \rightarrow \pi^*$ transition of conjugated double bond. The red-shift by 4-PPN is due to the extended conjugation than that of 2-PPN. Photoluminescence (PL) spectra were obtained from the excitation by the maximum absorption wavelength. Both 2-PPN and 4-PPN show blue PL emissions similarly around 439 and 435 nm in $CHCl_3$.

4. *Electroluminescence (EL) Properties*

The electroluminescence (EL) spectra of 2- and 4-PPN devices exhibited green emissions as shown in Figure 3. 2-PPN device 1, 2-PPN device 2 and 4-PPN device 1 showed respectively EL maximum at 509, 498 and 501 nm in the green region. The EL maximum

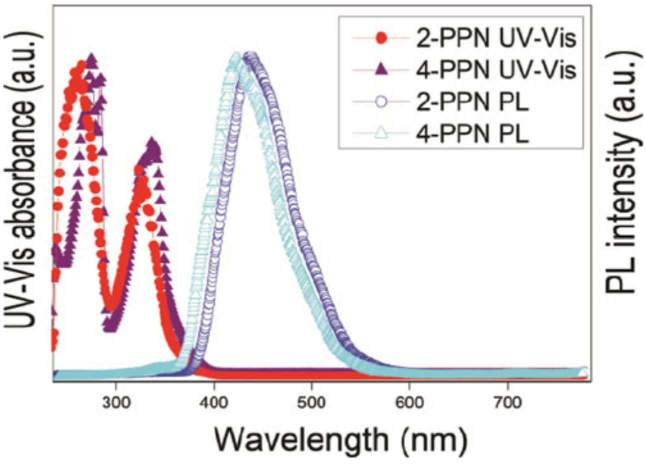


Figure 2. UV-Vis and PL spectra of 2-and 4-PPN in $CHCl_3$.

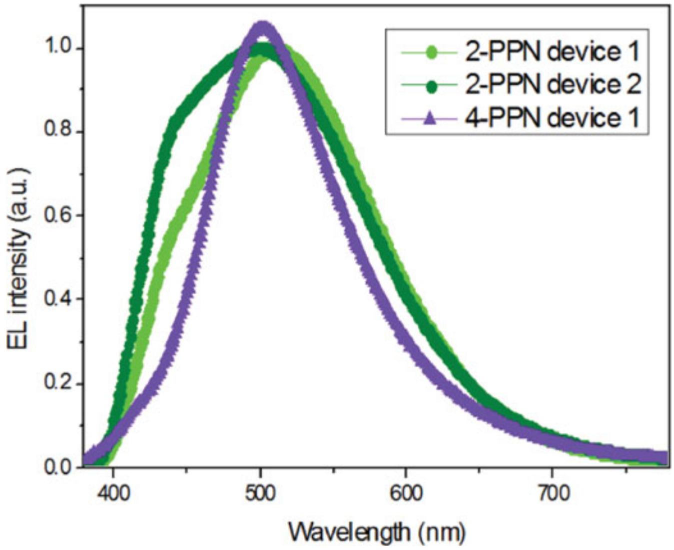


Figure 3. EL spectra of 2- and 4-PPN devices.

shows a red-shift compared with PL maximum. The blue PL emission changed to greenish blue EL emission, although the reasons are not clear at this point. However, the difference between EL and PL is the common phenomenon for this kind of chelate complex. And the two materials also showed red-shift EL maximum values than the corresponding PL values.

Figure 4 shows typical current (I)-voltage (V) characteristics for proposed device configurations. The turn-on voltages of 2-PPN device 1, 2-PPN device 2, and 4-PPN device 1, which is defined as the voltage when the luminance is 1 cd/m^2, were found to be respectively 4.2 V, 4.8 V and 4.0 V. 2-PPN device 1 showed the highest current density

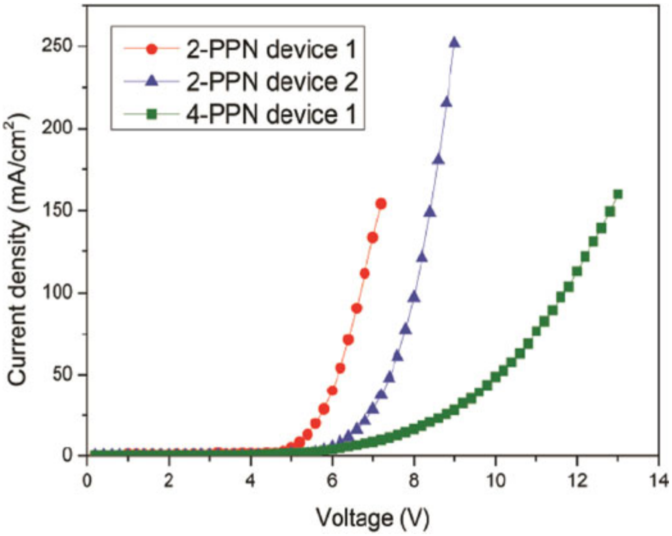


Figure 4. Current (I)-voltage (V) characteristics curves for proposed devices.

Table 2. Performance characteristics of PPN devices

Product	EL $_{max}$ (nm)	Voltage (V)	Luminescence (cd/m^2)	C.I.E. (x, y)
2-PPN device 1	509	7.0	340	0.303, 0.418
2-PPN device 2	498	8.2	480	0.303, 0.437
4-PPN device 1	501	13.0	440	0.256, 0.396

below 7.0 V, but 2-PPN device 2 showed more intensive current density over 8 V. In case of 4-PPN device 1 showed most slow increase of current density among the three devices.

The CIE value of 2- PPN device 1 changed from (0.303, 0.418) at 4.8 V to (0.268, 0.408) at 7.2 V. And 2- PPN device 2 also showed the change of CIE value from (0.303, 0.437) at 5.6 V to (0.255, 0.334) at 9.0 V. However, the CIE value of 4- PPN device 1 changed negligibly from (0.256, 0.396) at 9.0 V to (0.253, 0.400) at 13.0 V. The EL and CIE values are summarized in Table 2 [10].

Conclusion

EL materials of phosphine oxide-naphthoxazole structure such as 2-PPN and 4-PPN were first synthesized and characterized by ^{1}H-NMR, ^{13}C-NMR FT-IR, UV-Vis, EA, and XPS. 2-PPN and 4-PPN showed the thermal stability enough for EL device by TGA and DSC. While 2-PPN and 4-PPN reveal blue PL emissions, they emit greenish-blue lights by EL devices. CIE values of 2-PPN devices have changed by potential gradient, but 4-PPN device shows no change of CIE value with voltage increase. Although maximum luminance should be increased for EL applications, novel phosphine oxide-naphthoxazole materials are supposed to extend the scope of EL materials.

Acknowledgment

This paper was supported by the 2013 Inje University research grant.

References

[1] Tang, C. & VanSlyke, S. (1987). *Appl. Phys. Lett.*, *51*, 913.

[2] Aziz, H., Popovic, Z. D., Hu, N., Hor, A., & Xu, G. (1999). *Science*, *283*, 1900.

[3] Kraft, A., Grimsdale, A. C., & Holmes, A. B. (1998). *Angew. Chem. Int. Ed. Engl.*, *37*, 402.

[4] Sheats, J. R., Antoniadis, H., & Hueschen, M., *et al.* (1996). *Science*, *273*, 884.

[5] Chao, C. & Chen, S. (1998). *Appl. Phys. Lett.*, *73*, 426.

[6] Wu, Q., Esteghamatian, M., & Hu, N., *et al.* (1999). *Angew. Chem. Int. Ed. Engl.*, *38*, 985.

[7] Polikarpov, E., Swensen, J. S., Chopra, N., So, F., & Padmaperuma, A. B. (2009). *Appl. Phys. Lett.*, *94*, 223304.

[8] Kim, T., Murata, H., Okubo, T., & Mitani, T. (2004). *Science and Technology of Advanced Materials.*, *5*, 325.

[9] So, Y. & Heeschen, J. P. (1997). *J. Org. Chem.*, *62*, 3552.

[10] Salbeck, J., Yu, N., Bauer, J., Weissörtel, F., & Bestgen, H. (1997). *Synth. Met.*, *91*, 209.