



Synthesis and OLED Characteristics of Isomeric Phosphine Oxides Containing Naphthoxazole Moiety

Ik-Hwan Kim¹, Kyeong Hyeon Kim¹, Hyunhee Jo¹, Burm-Jong Lee^{1, *}, Dong-Eun Kim², and Hoon-Kyu Shin²

¹ Department of Chemistry, Inje University, Gimhae 50834, Korea ² National Center for Nanomaterials Technology, POSTECH, Pohang 37673, Korea

2-(2-(Diphenylphosphoryl)phenyl)naphtho[2,3-d]oxazole (**2-PPN**), 2-(3-(diphenylphosphoryl)phenyl) naphtho[2,3-d]oxazole (**3-PPN**), and 2-(4-(diphenylphosphoryl)phenyl)naphtho[2,3-d]oxazole (**4-PPN**) were synthesized as new light-emitting materials based on the phosphine oxide-naphthoxazole structure. The one-pot synthesis of the phosphine-naphthoxazole compound was achieved using PPA as a solvent and as a catalyst for the cyclization reaction. The phosphine structure was oxidized to phosphine oxide using aq. H_2O_2 , and the chemical structures were characterized via ¹H-NMR, ¹³C-NMR, FT-IR, UV-Vis, elemental analysis (EA) and X-ray photoelectron spectroscopy (XPS). TGA under an N₂ flow shows that the PPN derivatives were thermally stable at up to 400 °C. The photoluminescence (PL) spectra of the PPN derivatives in chloroform exhibited maximum wavelengths at around 439 nm for 2-PPN, 447 nm for 3-PPN, and 436 nm for 4-PPN. Electroluminescence (EL) devices with different configurations (1–4) were fabricated via vacuum deposition, and devices 1–4 emitted greenish-blue light with a maximum emission at around 509 (2-PPN), 498 (2-PPN), 528 (3-PPN) and 501 (4-PPN) nm.

Keywords: OLED, Phosphine Oxide-Naphthoxazoles, Photoluminescence, Electroluminescence.

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) have drawn a significant amount of interest due to their potential use in fullcolor flat-panel displays and in lighting sources. OLEDs offer the advantages of a wide viewing angle, highresponse velocity, low-power consumption, etc.^{1–6} However, OLEDs still need to be improved in terms of the emission efficiency in the blue color.

An efficient blue OLED can be produced if a blueemitting material with a high electron trap capacity can be fabricated. In such a case, the injected hole would be efficiently recombined with trapped electrons in the emitting material. As such, an ambipolar phosphine oxide material has been previously shown to have a high-power efficiency in its blue phosphorescence.⁷

Accordingly, we have designed new phosphine oxideoxazole compounds where the oxygen, nitrogen, and phosphorus atoms are combined with naphthalene and three phenyls to produce a blue emission with the desired electron-trapping properties.^{8,9} Recently, carbazolyl and aryl phosphine oxide (APO) based ambipolar host materials for blue electrophosphorescence were investigated via a density functional theory.¹⁰

To this end, we have extended the scope of OLED materials by newly synthesizing isomeric phosphine oxidenaphthoxazole derivatives of 2-, 3-, 4-PPN, and we characterized them in terms of their structures and physicochemical properties. As is typical, their isomericallyfeatured OLED properties were also investigated.

2. EXPERIMENTAL DETAILS

2.1. Materials

3-Amino-2-naphthol, nickel(II)bromide, 2-(diphenyl phosphino) benzoic acid (>97%), 4-(diphenyl phosphino) benzoic acid (>97%), chlorodiphenyl-phosphine, polyphosphoric acid (PPA), and N-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich Chemical Co. Sodium hydroxide was obtained from SAMCHUN Chemical; ethyl 3-bromobenzoate from TCI, 2,2'-bipyridine from

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^{*}Author to whom correspondence should be addressed.

Alfa Aesar; hydrogen peroxide 30% in H₂O from Junsei Chemical; and *p*-toluenesulfonic acid from KANTO Chemical. The solvents were purified using normal procedures and were handled under a moisture-free atmosphere.

2.2. Instrumentation

¹H-NMR and ¹³C-NMR spectra were obtained using a LC-NMR spectrometer (VNMRS 500, Varian). The optical absorption spectra were measured using a Shimadzu UV-2501 PC Spectrometer. The PL spectrum was taken using a Perkin-Elmer LS45 luminescence spectrometer. The current density–voltage–luminance (I-V-L) characteristics and the efficiency were measured using an IVL 300 series device (JBS Inc.).

2.3. Synthesis of PPN Derivatives 2.3.1. 2-(2-(diphenylphosphoryl)phenyl)naphtho [2,3-d]oxazole (2-PPN)

Figure 1 shows the synthetic scheme for 2-PPN. The synthesis of the PPN derivatives followed closely-related procedures.^{11,12} After 3-amino-2-naphthol (0.159 g, 1.0 mmol), 2-(diphenylphosphino)benzoic acid (0.306 g, 1.0 mmol) and *p*-toluenesulfonic acid (0.190 g, 1.0 mmol) were dissolved in 30 ml toluene, the mixture was stirred for 15 hours at 150 °C under an N₂ atmosphere in a round bottom flask. The reaction progress was monitored



Figure 1. Synthetic scheme of 2-PPN.

J. Nanosci. Nanotechnol. 17, 3298–3303, 2017

via TLC. After cooling to ambient temperature, the mixture was extracted with toluene, and the organic solution was collected and evaporated. Then the crude intermediate was stirred in 10 mL CH_2Cl_2 , and then H_2O_2 (1.2 mL, 10 mmol, 30%) was added drop-wise while stirring at room temperature. The organic solution was separated and washed with deionized water, and the extract was evaporated to dryness, affording to a pale yellow solid. This residue was dissolved in $CHCl_3$ and was added to methanol in order to obtain a solid precipitate. The crude product was chromatographed on silica gel with $CHCl_3$:ethyl acetate, 5:1 to obtain pure 2-PPN.

Anal.Calc.(%) for $C_{29}H_{20}NO_2P$, C:78.19, H:4.53, N:3.14, O:7.18. Found (%, XPS) C:77.93, H:4.69, N:2.95, O:6.46. ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.18–8.21 (*m*, 2H), 7.99 (*s*, 1H), 7.90 (*q*, δ = 11.5 Hz, 1H), 7.78– 7.82 (*m*, 4H), 7.73–7.76 (*m*, 4H), 7.62 (*q*, δ = 7.5 Hz, 1H), 7.42–7.47 (*m*, 6H), 7.43 (*s*, 1H). ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 164.02, 149.22, 141.18, 135.37, 135.29, 133.66, 133.25, 132.89, 132.40, 132.04, 131.71, 131.67, 131.60, 131.59, 131.48, 131.46, 131.26, 131.03, 130.98, 130.93, 130.84, 128.26, 128.17, 125.41, 124.55, 117.61, 106.57. FT-IR (KBr, cm⁻¹) 1549 (C=N), 1456 (P–C), 1435 (aromatic C=C), 1190 (stretch P=O), 1113 (C–O).

2.3.2. Ethyl-3-(diphenylphosphoryl)benzoate (1)

NiBr₂(bpy) was prepared according to a previouslyreported method.¹³ A mixture of ethyl 3-bromobenzoate (1.601 ml, 10 mmol), chlorodiphenylphosphine (1.85 ml, 10 mmol) and NiBr₂(bpy) were dissolved in 5 ml NMP (N-methyl-2-pyrrolidone). Zinc dust (1.1 g, 16 mmol) was added portion-wise in a few minutes. The solution was heated under nitrogen to 110 °C, and after 3 hours, the reaction was finished. The solution was then allowed to cool at room temperature and was subsequently filtered.

The filtered solution was evaporated and dried under a vacuum, and the dried precipitate was dissolved in 10 mL CH₂Cl₂. Then, H₂O₂ (2 mL, 30%) was added dropwise while stirring at room temperature. The solution was extracted 3 times with water, and then the organic layer was collected and evaporated.

FT-IR (KBr, cm⁻¹) 3057 (stretch, $-CH_3$), 2991 (stretch, $-CH_2$ -), 1717 (C=O), 1436 (bend, $-CH_2$ -), 1113 (bend, $-CH_3$).

2.3.3. Sodium-3-(diphenylphosphoryl)benzoate (2)

Sodium 3-(diphenylphosphoryl)benzoate was synthesized via saponification of ethyl 3-(diphenyl phosphoryl)benzoate. A methanolic solution of NaOH (2–3 N, 1–4 equiv.) was added to a solution of ester (1 equiv.) in a CH_2Cl_2/CH_3OH (9:1) mixture, with the final concentration of alkali being about 0.3 N. After stirring for 10 min, the solvents were then removed using an evaporator. FT-IR (KBr, cm⁻¹) 1721 (C=O).

3299

Synthesis and OLED Characteristics of Isomeric Phosphine Oxides Containing Naphthoxazole Moiety

Kim et al.

2.3.4. 2-(3-(diphenylphosphoryl)phenyl) naphtho[2,3,-d]oxazole (3-PPN)

Figure 2 shows the synthetic scheme of 3-PPN. 3-Amino-2-naphthol (0.159 g, 1.0 mmol) and sodium 3-(diphenylphosphoryl)benzoate (0.344 g, 1.0 mmol) were dissolved in 30 mL polyphosphoric acid (PPA), and the mixture was stirred for 15 hours at 150 °C under a nitrogen atmosphere. The progress of the reaction was monitored via TLC. The crude solution was stirred with water 3 times, filtered, and extracted with CHCl₃ to collect and evaporate the organic layer. The crude product was chromatographed on silica gel with CHCl₃:ethanol, 50:1 to obtain pure 3-PPN.

Anal. Calc.(%) for $C_{29}H_{20}NO_2P$, C:78.19, H:4.53, N:3.14, O:7.18. Found(%) C:76.42, H:4.69, N:4.65, O:7.69. ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.66–8.68 (*m*, 2H), 8.53 (*d*, *J* = 12 Hz, 1H), 8.19 (*s*, 1H), 7.89–8.00 (*m*, 4H), 7.73–7.77 (*m*, 4H), 7.68 (*t*, *J* = 6.7 Hz, 1H), 7.60 (*t*, *J* = 7.2 Hz, 1H), 7.46–7.54 (*m*, 6H). ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 163.80, 149.56, 141.72, 135.34, 134.55, 133.73, 132.30, 132.12, 132.08, 132.04, 131.95, 131.93, 131.86, 131.51, 131.49, 131.39, 131.37, 129.30, 129.20, 128.78, 128.69, 128.54, 128.45, 127.92, 127.45, 125.67, 124.81, 117.61, 106.54. FT-IR (KBr, cm⁻¹): 1549 (C=N), 1456 (P-C), 1435 (aromatic C=C), 1190 (stretch P=O), 1113 (C–O).







Figure 3. Synthetic scheme of 4-PPN.

2.3.5. Synthesis of 2-(4-(diphenylphosphoryl)phenyl) naphtho[2,3-d]oxazole (4-PPN)

Figure 3 shows the synthetic scheme of 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 PPA (30 mL). The mixture was heated at 150 °C for 15 hours under an N₂ atmosphere, and the progress of the reaction was confirmed via TLC. After the reaction mixture had cooled, the reaction solution was extracted with CHCl₃. The organic layer was dried using MgSO₄ and was then filtered. The crude intermediate was stirred in 10 mL CH₂Cl₂ in a round bottom flask, and H₂O₂ (1.2 mL, 10 mmol, 30%) was then slowly added into the mixture while stirring at room temperature. The organic layer was separated and washed with water, and the extract was evaporated to dryness, affording a pale yellow solid. The residue was dissolved in CHCl₃ and was added to methanol in order to obtain a solid precipitate. The crude product was chromatographed on silica gel with CHCl₃:ethyl acetate, 5:1 to obtain pure 4-PPN.

Anal.Calc.(%) for $C_{29}H_{20}NO_2P$, 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. ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.41–8.43 (m, 2H), 8.23 (s, 2H), 7.96–8.02 (m, 2H), 7.86–7.90 (m, 4H), 7.70–7.74 (m, 4H), 7.47–7.61 (m, 6H). ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 163.77, 149.60, 141.71, 136.98 (3C), 136.17 (2C), 132.68, 132.60, 132.28, 132.27, 132.12, 132.04, 131.98, 131.57, 131.45, 130.05, 130.02, 128.75, 128.65, 128.59, 127.94, 127.92, 127.84, 125.78, 124.88, 117.84, 106.59. FT-IR (KBr, cm⁻¹): 1543 (C=N), 1486 (P–C), 1437 (aromatic C=C), 1179 (stretch P=O), 1112 (C–O).

2.4. OLED Device Fabrication

The OLED devices were fabricated on glass substrates. First, the organic layers were vacuum-deposited using thermal evaporation at a vacuum base pressure of 2×10^{-7} torr. The multilayer structure consists of the following layers (as shown in Table I): Indium tin oxide (ITO) as the anode; 1,3-bis(1-naphthylphenylamino) biphenyl (NPB) as a transport layer (40 nm); 2-, 3-, or 4-PPN as an emitting layer (50 nm); 1,3,5-tris(N-phenylbenzimidizol-2-yl)benzene (TPBi) as an electron transport layer (30 nm);

J. Nanosci. Nanotechnol. 17, 3298-3303, 2017

Kim et al.

Table I.	Configuration of the OLED devices.
Device	Structure
1	ITO/NPB (50 nm)/2-PPN (50 nm)/Liq (0.5 nm)/Al (120 nm
2	ITO/NPB (50 nm)/2-PPN (50 nm)/Alq ₃ (15 nm)/ Liq (0.5 nm)/Al (120 nm)
3	ITO/NPB (40 nm)/3-PPN (50 nm)/TPBi (30 nm)/ Liq (0.5 nm)/Al (120 nm)
4	ITO/NPB (40 nm)/4-PPN (50 nm)/TPBi (30 nm)/ Liq (0.5 nm)/Al (120 nm)

8-hydroxyquinolate lithium (Liq) as an electron injection layer (0.5 nm); and Al as a cathode (120 nm).



Figure 5. UV-vis spectra of PPN derivatives.

3. RESULTS AND DISCUSSION

3.1. Structure Determination and PL Properties

The chemical structures of 2-PPN, 3-PPN and 4-PPN were determined via ¹H-NMR, ¹³C-NMR, FT-IR, and elemental analysis. The FT-IR spectra (Fig. 4) of the PPN derivatives confirmed the newly-formed C=N bond (1549 cm⁻¹) of the oxazole ring.

The ¹H-NMR spectra showed aromatic peaks only from around 7 to 9 ppm. The formation of the oxazole ring was also confirmed by the ¹³C-NMR spectra. ¹³C peaks



Figure 5 shows the UV-absorption spectra of the PPN derivatives, which was measured in $CHCl_3$, exhibiting a maximum absorption of around 266 (2-PPN), 272 (3-PPN) and 276 (4-PPN) nm. The photoluminescence (PL) spectra (Fig. 6) were obtained from the excitation by the maximum absorption wavelength. The PPN derivatives similarly show blue PL emissions around 439, 447 and 436 nm in $CHCl_3$.



Figure 4. FT-IR spectra of 2-PPN (top), 3-PPN (middle) and 4-PPN (bottom).

J. Nanosci. Nanotechnol. 17, 3298-3303, 2017

livered by Ingenta to: State University Thermal Properties by TGA and DSC

The thermal properties of the PPN derivatives were investigated via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. The TGA and DSC spectra are shown in Figure 7. The decomposition of 2-PPN, 3-PPN and 4-PPN begins at about 427 °C, 426 °C and 393 °C, respectively. The results of the TGA indicate that the PPN derivatives possess a high thermal stability, which may be an advantage in OLED fabrication. The melting points (T_m) were observed at 217.5 °C (2-PPN), 259.6 °C (3-PPN) and 291.8 °C (4-PPN).



Figure 6. PL spectra of PPN derivative.

3301



Figure 7. TGA (a) and DSC (b) curves of the PPN derivatives. On: Tue, 0 Copyright: American Scie

3.3. Electroluminescent (EL) Properties

To illustrate the EL properties of the PPN derivatives, typical multilayer OLED devices were fabricated using 2-PPN, 3-PPN and 4-PPN as the emitting layer (Table I). Figure 8 shows the EL spectra of devices 1–4. The EL devices emit green light with an emission maximum at 509, 498, 528 and 501 nm, respectively. The EL maximum shows a redshift when compared to the PL maximum. Thus, the blue PL emission changed to a greenish-blue EL emission as the difference between EL and PL is common for this kind of chelate complex. All compounds also showed different maximum values for the PL and EL due to differences in the conjugation length of the PPN derivatives. Figure 9 displays the current density–voltage–luminance (I-V-L)characteristics of the devices.

Device 1 uses 2-PPN as the emitter, and it exhibits a turn-on voltage of 5.0 V, current density of 180 mA/cm² and maximum brightness of 340 cd/m² at 7.0 V. Device 2 uses 2-PPN as the emitter together with Alq₃, and it shows a turn-on voltage of 6.0 V, current density of 240 mA/cm² and maximum brightness of 480 cd/m² at 9.0 V. Similarly, Device 3 uses 3-PPN as the emitter and shows a turn-on voltage of 10.0 V, current density of 44.65 mA/cm² and maximum brightness of 62.11 cd/m² at 20.0 V. Device 4 uses 4-PPN as the emitter and shows a turn-on voltage



Figure 8. EL spectra of OLED devices.

of 5.0 V, current density of 160 mA/cm² and maximum brightness of 440 cd/m² at 13.0 V.

Although the OLED devices using the PPN derivatives had a relatively low luminance efficiency, we expect that the EL efficiency could be further improved



Figure 9. Current density versus applied voltage (a) and luminance versus applied voltage (b) of the EL devices.

J. Nanosci. Nanotechnol. 17, 3298-3303, 2017

Kim et al.

by searching for other buffer layers with the appropriate compounds in order to obtain high-efficiency devices.

4. CONCLUSION

We investigated the properties of OLED devices using newly synthesized PPN derivatives as the emitter. The PPN derivatives exhibited blue PL emissions at around 439 nm (2-PPN), 447 nm (3-PPN), 436 nm (4-PPN). EL Devices 1–4 employing the four different PPN derivatives emitted greenish-blue lights with maximum emission at around 509 nm, 498 nm, 528 nm and 501 nm, respectively. The devices with the 2-PPN and 4-PPN showed a better performance than that with a 3-PPN when used as OLED emitters.

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