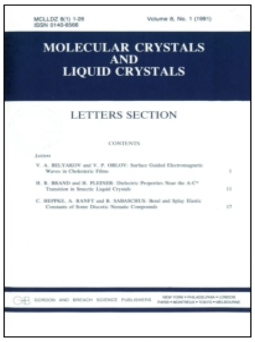

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Synthesis of phosphine oxides with tris(benzoxazole/benzothiazole) moieties and their OLED characteristics

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ABSTRACT

We have developed a series of phosphine oxides with heterocycles for the light-emitting materials of various colors. In this study, we report novel phosphine oxides with tris(benzoxazole/benzothiazole) moieties, such as (4-(benzo[d]thiazol-2-yl)phenyl)phosphine oxide (4-TBTPO) and tris(4-(benzo[d]oxazol-2-yl)phenyl)phosphine oxide (4-TBOPO). The cyclization reactions were carried out from 4,4′,4″-phosphoryltribenzoic acid and 2-aminobenzenethiol or 2-aminophenol with tetrabutylammonium bromide and triphenyl phosphite as catalysts. The structures and thermal properties were investigated by ^{1}H-NMR, ^{13}C-NMR, FT-IR, UV-Vis, TGA and DSC. The OLED devices of ITO/MoOx(30 nm)/NPB(600 nm)/4-TBTPO or 4-TBOPO(200 nm)/Alq_3(300 nm)/Liq(10 nm)/ Al(120 nm) showed yellow-green emissions at (0.429∼0.529) and (0.406∼0.563) of CIE color coordinates, respectively.

KEYWORDS

phosphine oxide; benzoxazole; benzothiazole; OLED; yellow-green emission

Introduction

Organic electrophosphorescence devices have attracted intense interests because their intrinsic efficiencies may be up to four times higher as the fluorescence ones [1]. In the design of highly efficient phosphorescent devices, the selection of a proper material for each layer is also of great importance. In accordance with the efficient phosphorescent materials, bipolar structures of phosphine oxides with heterocycles have caught great attention [2,3]. A noticeable advantage of using a bipolar host is the improvement of carrier mobility and balance of electron and hole fluxes in the emitting layer [4]. On the other hand, two intrinsic criteria have restricted the development of blue host materials: (1) their triplet energy (ET) level must be higher than blue dopant to prevent exothermic reverse energy transfer from guest to host and confine the triplet exciton within the emitting layer, and (2) in order to extend the operational lifetime of the device, the blue host must possess good morphological and chemical stabilities to form stable amorphous films [5–7]. On these reasons the new structures of phosphine oxides with heterocycles are expected to expand the scope of OLED materials. We have also reported a series of isomeric triphenylphosphine oxides with heterocycles and found the characteristic EL properties [8,9]. Particularly, the synthesis of heterocycles

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with benzoxazole and benzothiazole was efficiently carried out by one-pot cyclization [10]. In this study, we synthesized novel phosphine oxide materials with three arms of heterocycle moieties such as tris(4-(benzo[d]thiazol-2-yl)phenyl)phosphine oxide (4-TBTPO) and tris(4-(benzo[d]oxazol-2-yl)phenyl)phosphine oxide (4-TBOPO). The three-armed structures are expected to show enhanced bipolarity and amorphous aggregate morphology in films. The characterization of the materials and their OLED properties are presented.

Experimental

1. Material

2-Aminophenol and 2-aminothiophenol were purchased from Aldrich and used without further purification. Triphenyl phosphite, tetrabutylammonium bromide and tri(p-tolyl)phosphine were purchased from TCI, potassium permanganate from DAEJUNG and sodium carbonate from SAMCHUN Chemical. All the purchased chemicals were also used without further purification.

2. Synthesis

2.1. Synthesis of tris(4-(benzo[d]thiazol-2-yl)phenyl)phosphine oxide (4-TBTPO)

4,4′,4″-Phosphoryltribenzoic acid (TCPO) was firstly prepared from oxidation of tri(p-tolyl)phosphine by potassium permanganate. Tri(p-tolyl)phosphine (0.3 g, 1.0 mmol), sodium carbonate (0.24 g, 3.0 mmol) and potassium permanganate (0.47 g, 3.0 mmol) were added to water (30mL). The mixture was heated at 120°C for 5 h with reflux condenser. After filtering the reaction mixture, dilute aq. HCl was slowly added to the filtrate. The precipitates were recrystallized from methanol. The structure of TCPO could be simply confirmed by spectroscopic methods. Then TCPO (0.42 g, 1 mmol), triphenyl phosphite(0.78 mL, 3 mmol), tetrabutylammonium bromide (0.96 g, 3 mmol), 2-aminothiophenol (0.32 mL, 3 mmol) were added to flask with reflux condenser and heated at 120°C for 3h. The progress of reaction was monitored by TLC. After the completion of reaction, the product was precipitated from the solution by adding methanol and filtered. Then the product was dissolved in $CHCl_3$, added anhydrous $MgSO_4$, and stirred at room temperature for 4h. Filtered and evaporated the solvents to get a yellow solid. 4-TBTPO; Yield 39%; EA Found (%) C 68.20, N 6.18, O 2.20, H 3.32, S 13.86; Calcd. (%) C 69.11, N 6.20, O 2.36, H 3.57, S 14.19; ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.23∼8.24(m, 6H), 8.10∼8.11(d, 2H), 7.94∼7.92(d, 1H), 7.90∼7.86(m, 6H), 7.54∼7.51(m, 4H), 7.45∼7.42(m, 4H), 7.26(s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 166.24, 154.11, 137.16, 135.26, 134.63, 133.74, 132.81 132.73, 127.72, 127.68, 126.56, 123.64, 121.77.

2.2. Synthesis of tris(4-(benzo[d]oxazol-2-yl)phenyl)phosphine oxide (4-TBOPO)

The synthesis of tris(4-(benzo[d]oxazol-2-yl)phenyl)phosphine oxide was progressed similarly to the synthesis of 4-TBTPO. The synthesized TCPO (0.42 g, 1 mmol), triphenyl phosphite(0.78 mL, 3 mmol), tetrabutylammonium bromide (0.96 g, 3 mmol), 2-aminotriphenol (0.42 g, 3 mmol) were added to flask with reflux condenser and heated at 120°C for 3h. The progress of reaction was monitored by TLC. After the completion of reaction, the product was precipitated from the solution by adding methanol and filtered. Then the product was dissolved in $CHCl_3$, added anhydrous $MgSO_4$, and stirred at room temperature for 4h. Filtered and evaporated the solvents to get a yellow solid. 4-TBOPO; Yield 36%; EA Found (%) C 73.01, N 3.90, O 10.71, H 6.30; Calcd. (%) C 74.40, N 3.84, O 10.16, H 6.67; ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.43~8.40(m, 6H), 7.94~7.90(m, 6H), 7.82~7.79(m, 3H), 7.64~7.60(m, 3H), 7.43~7.37(m, 5H), 7.26(s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 161.59, 150.86, 141.95, 135.12, 134.30, 132.67, 132.59, 130.91, 130.87, 127.90, 127.67, 125.83, 124.98, 120.39, 110.76.

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. UV-Vis absorption spectra were measured by a UV-Vis Spectrometer (ShimadzuUV-3100S). The characteristics of the current density-voltage-luminance (I-V-L) were measured by IVL 300 series (JBS Inc.).

4. Device fabrication

The OLED 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. Molybdenum trioxide (MoOx) as a charge generation layer, 1,4-bis(1-naphthylphenylamino)biphenyl (NPB) as a hole transport layer, 4-TBTPO or 4-TBOPO as an emitting layer, 8-hydroxyquinolate aluminium (Alq_3) as electron transport layers, 8-hydroxyquinolate lithium (Liq) as an electron injection layer, and Al as a cathode were respectively employed. Device 1: ITO / MoOx [30] / NPB [600] / 4-TBOPO [200] / Alq_3 [300] / Liq [10] /Al [120nm] and Device 2: ITO / MoOx [30] / NPB [600] / 4-TBTPO [200] / Alq_3 [300] / Liq [10] /Al [120nm].

Results and discussion

1. Synthesis and structure determination

The ring structures of benzoxazole and benzothiazole were synthesized from cyclization reaction of 4,4′,4″-phosphoryltribenzoic acid (TCPO) with corresponding 2-aminophenol and 2-aminothiophenol. TCPO was firstly prepared from oxidation of tri(p-tolyl)phosphine by $KMnO_4$. The synthetic scheme is shown in Figure 1. Although a few cyclization methods were attempted for higher yield and easy purification, the catalytic system using triphenyl phosphite and tetrabutylammonium bromide was most efficient in this case [10].

The structures of 4-TBTPO and 4-TBOPO were confirmed by FT-IR, ^{1}H-NMR, ^{13}C-NMR, and EA. The FT-IR spectra of 4-TBTPO and 4-TBOPO show the evanishment of carboxyl group (1695 cm^{-1}). The bands from P=O bonds were respectively found at 1164 cm^{-1} (TCPO), 1189 cm^{-1} (4-TBTPO) and 1199 cm^{-1} (4-TBOPO). The formation of C=N bonds was confirmed from the bands at 1598 cm^{-1} (4-TBTPO) and 1545 cm^{-1} (4-TBOPO). The presence of C-O bond was proved by the bands at 1117 cm^{-1} (4-TBTPO) and 1118 cm^{-1} (4-TBOPO). ^{1}H-NMR spectra showed aromatic peaks ranged from 7.26 to 8.23 ppm in 4-TBTPO and from 7.26 to 8.43 ppm in 4-TBOPO. The chemical shifts of the peaks were presented in Experimental section. The ring formation of benzoxazole and benzothiazole was also confirmed by ^{13}C-NMR spectra from 166.24 ppm (4-TBTPO) and 161.59 ppm (4-TBOPO), which originates from C of C=N bonds. Elemental analysis showed that the elemental compositions of 4-TBTPO and 4-TBOPO were agreed with calculated values as presented in Experimental section.

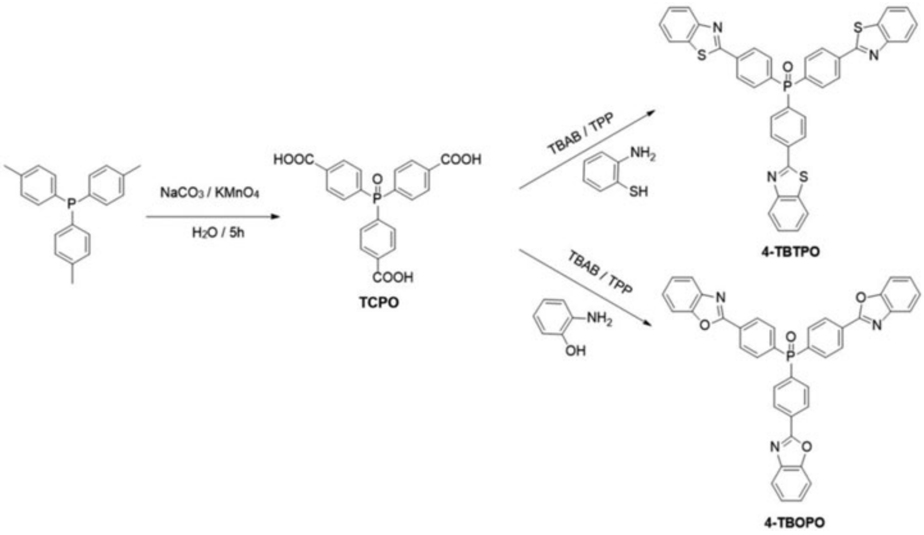

Figure 1. Synthetic scheme of 4-TBTPO and 4-TBOPO.

2. Thermal properties by DSC and TGA

The thermal stability of OLED materials is very important, because the durability of multilayer devices significantly depends on the thermal stability of organic materials. We confirmed the thermal properties of 4-TBTPO and 4-TBOPO by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) as summarized in Table 1. The melting points of 4-TBTPO and 4-TBOPO were respectively determined as 278 and 283°C by DSC. Thermal degradation of 4-TBTPO began around 400°C, while 4-TBOPO started the degradation from around 220°C. The temperature as of 50% weight loss was found as 565°C (4-TBTPO) and 475°C (4-TBOPO), respectively. The TGA curves are shown in Figure 2. The high melting points and thermal stability of 4-TBTPO and 4-TBOPO indicate enough to fabricate stable OLED devices.

3. Electroluminescence (EL) properties

The UV absorption spectra of 4-TBTPO and 4-TBOPO are shown in Figure 3. 4-TBTPO shows somewhat broader band and longer maximum absorption wavelength (λ_{max}) than 4-TBOPO. The structural difference between 4-TBTPO and 4-TBOPO is only the O and S in heterocycles. Therefore, the different electronic contributions to the aromatic heterocycles are mainly thought to attribute to the absorption patterns.

Table 1. Thermal properties of 4-TBTPO and 4-TBOPO.

		TGA	
Compound	DSC T_m[a] (°C)	T_d[b] (°C)	Residue (wt. %)
4-TBTPO	278	565	5.35
4-TBOPO	283	475	10.68

[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).

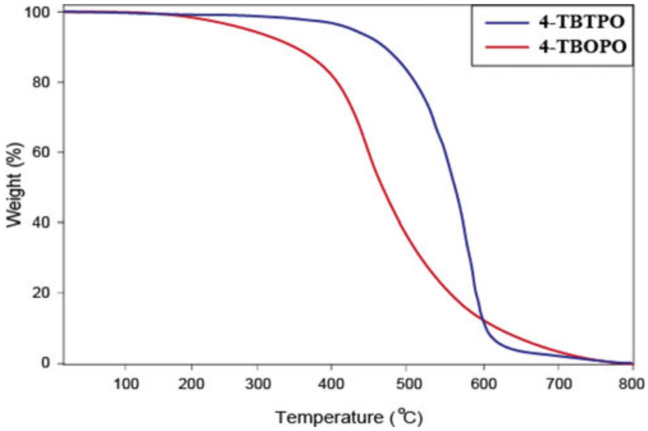

Figure 2. TGA curves of 4-TBTPO and 4-TBOPO.

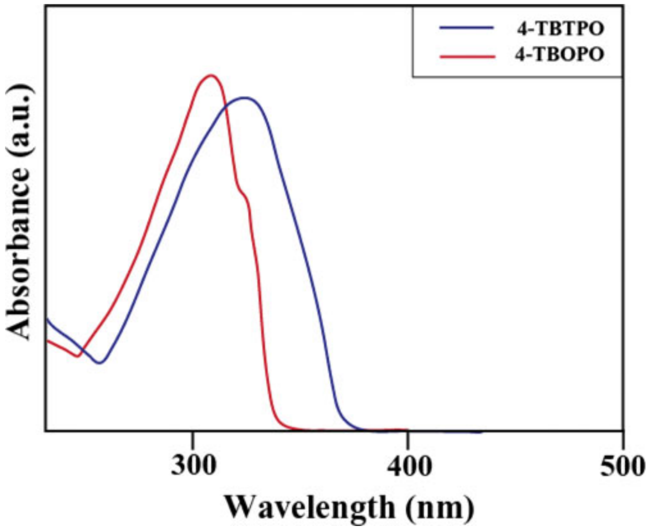

Figure 3. UV-Vis spectra of 4-TBTPO and 4-TBOPO in $CHCl_3$.

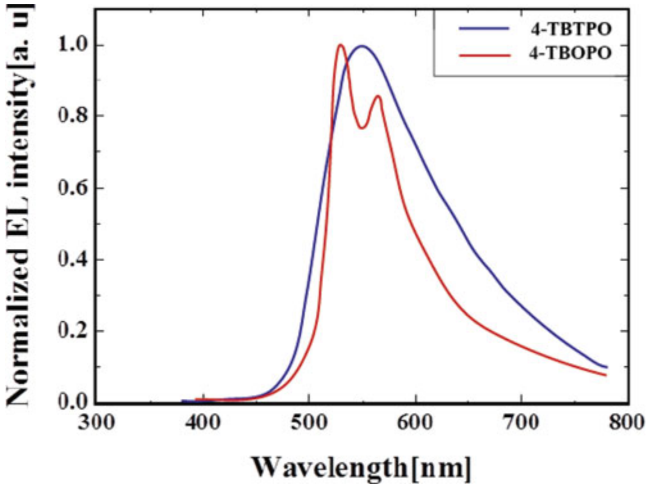

Figure 4. EL spectra of 4-TBTPO and 4-TBOPO devices.

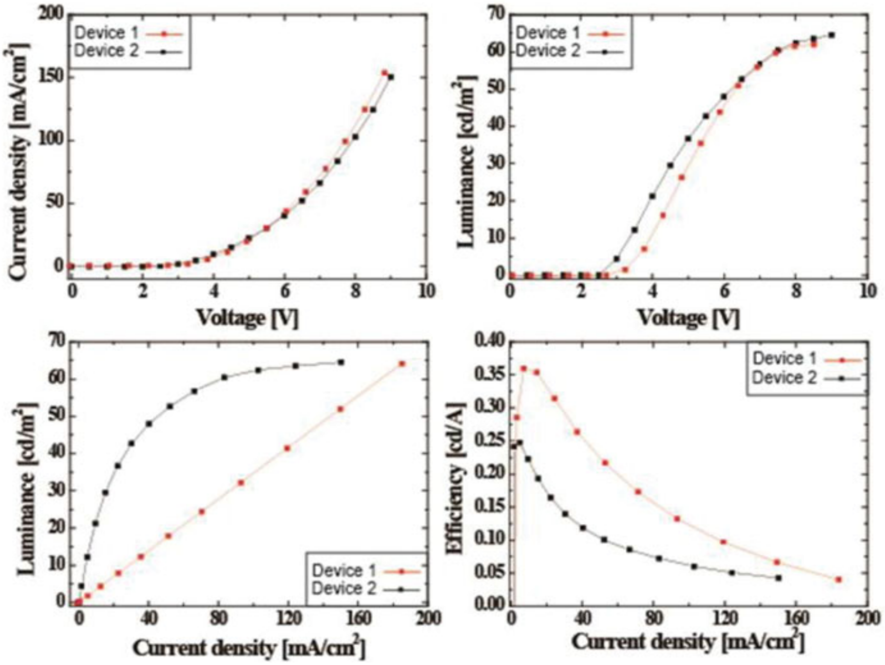

Figure 5. Current density-voltage-luminance (I-V-L) characteristics of 4-TBTPO and 4-TBOPO.

The EL device 1 was fabricated with the structure of ITO / MoOx[30] / NPB[600] / 4-TBOPO[200] / Alq_3[300] / Liq[10] /Al[120nm]. Device 2 also has same structure as device 1 with only differently using 4-TBTPO instead of 4-TBOPO. Figure 4 shows the EL spectra of device 1 (4-TBOPO) and device 2 (4-TBTPO). The maximum emissions of the devices are measured on yellow-green regions of λ_{max} 550 nm (4-TBTPO) and 530 nm (4-TBOPO), respectively. In case of 4-TBTPO, the EL spectra are found red-shifted about 20 nm compared with 4-TBOPO as also found in the UV absorption spectra. Another difference is the pattern of EL peak, that is, while device 1 (4-TBOPO) shows split peaks, device 2 (4-TBTPO) does one broad peak. Although the difference of peak pattern is thought to originate from different intermolecular aggregates of the compounds in films, the detail clarification on the EL patterns is not clear at this point.

The current density-voltage-luminance (I-V-L) characteristics of the device are shown in Figure 5. The device 1 showed a maximum current density of 150 mA/cm^2. The maximum luminance exhibited about 65 cd/m^2 at 9V. The two devices showed very similar I-V-L curves, though device 2 started EL emission at somewhat low potential. A large difference between the two devices was found in luminance-current density curve. Although device 1 shows a linear increase of luminance with the current density, the device 2 shows early saturation of luminance at low current density. In case of device 2, the efficiency also rapidly decreased with the increase of current density.

The CIE value of device 1 (4-TBOPO) changed from (0.406, 0.563) at 5 V to (0.410, 0.553) at 8V. And device 2 (4-TBTPO) also showed the change of CIE value from (0.429, 0.529) at 6 V to (0.424, 0.527) at 9V. However, the difference of CIE values along with applied voltages is a very little, the devices are thought to show stable EL emissions. The EL properties above are summarized in Table 2.

Table 2. EL properties of 4-TBTPO and 4-TBOPO.

Compound	EL color	λ_{max} (nm)	Max. luminance (cd m^{-2}) (applied voltage, V)[a]	CIE coordinate
4-TBOPO	yellow-green	530	62 (8)	(0.406, 0.563) at 5V
4-TBTPO	yellow-green	550	65 (9)	(0.429, 0.529) at 6V

[a] EL device structure: ITO / MoOx[30] / NPB[600] / 4-TBOPO[200] / Alq_3[300] / Liq[10] /Al[120nm]

Conclusion

We have synthesized novel OLED materials, 4-TBTPO and 4-TBOPO, based on three–armed phosphine oxide with aromatic heterocycles. The chemical structure was proved by ^{1}H-NMR, ^{13}C-NMR, FT-IR, UV-Vis and EA. The materials showed high melting points and good thermal stability. It means that all of compounds have thermal stability enough to make the device under vacuum evaporation. The EL devices employed 4-TBTPO and 4-TBOPO as emitting layers were fabricated, and both showed the maximum luminance of 65 cd/m^2 at the current density of 150 mA/cm^2.

Acknowledgment

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