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### Structure–property relationship in high triplet energy host materials with a phenylcarbazole core and diphenylphosphine oxide substituent

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#### ABSTRACT

A series of high triplet energy host materials with a carbazole core and a diphenylphosphine oxide substituent were synthesized and the effect of the substitution position on the photophysical properties and device performances of the host material was investigated. The substitution position of the diphenylphosphine oxide on the phenyl ring was changed and the substitution at ortho position of the phenyl ring induced the intramolecular charge transfer complex formation. The intramolecular charge transfer complex formation in the ortho substituted compound improved the current density. A maximum quantum efficiency of 20.4% was obtained in the phenylcarbazole host material with the phosphine oxide at para position of the phenyl group and the efficiency was degraded in the ortho substituted host.

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#### 1. Introduction

The development of deep blue phosphorescent organic light-emitting diodes (PHOLEDs) is very important to improve the power consumption of the organic light-emitting diode (OLED) display due to the low quantum efficiency of the current fluorescent OLED. The quantum efficiency can be quadrupled using the PHOLED instead of the fluorescent OLED and the power consumption of the OLED display can be significantly reduced [1].

There are several ways to improve the quantum efficiency of the deep blue PHOLED. One of the most efficient approaches is to develop high triplet energy host materials for balanced hole and electron injection in the emitting layer [2–24]. Carbazole based host materials have been widely used as the high triplet energy host material, but the strong hole transport property of the carbazole type host material limited the quantum efficiency of the blue PHOLED [2,3]. Silane type host materials were also applied as the host material in the blue PHOLED, but

\* Corresponding author. Tel./fax: +82 31 8005 3585. E-mail address: leej17@dankook.ac.kr (J.Y. Lee). the deep highest occupied molecular orbital (HOMO) level of the silane based host material blocked the hole injection from a hole transport layer to the emitting layer [4,5]. Additionally, the poor thermal stability of the silane based host material destabilized the morphology of the evaporated host film. A silane modified carbazole host was also synthesized as the high triplet energy host material and it showed good electrochemical stability [6,7]. However, the host material had strong hole transport property and it was difficult to balance holes and electrons in the emitting layer. Phosphine oxide type host materials have been developed as electron transport type host materials and they were effective to improve the quantum efficiency of the blue PHOLED in spite of strong electron transport character of the phosphine oxide type host [8-19]. The charge transport property of the phosphine oxide type host material could be improved by combining the phosphine oxide group with the phenylcarbazole group [10,11]. The phenylcarbazole based host material modified with two diphenylphosphine oxide groups was effective as the host material for the deep blue PHOLED and a high quantum efficiency over 18% was reported in the deep blue PHOLED due to balanced

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In this work, the effect of the substitution position of the phosphine oxide on the physical properties of the host material and device performances of the deep blue PHOLED were investigated. The diphenylphosphine oxide was attached to the ortho, meta and para position of the phenyl group in the phenylcarbazole unit. It was demonstrated that the para substitution is better than ortho or meta substitution in terms of quantum efficiency. A high quantum efficiency of 20.4% was demonstrated from the deep blue PHOLED with the phenylcarbazole based host substituted at para position of the phenyl group.

#### 2. Experimental

#### 2.1. Materials and measurements

9H-carbazole, *n*-butyllithium, chlorodiphenylphosphine, *N*-bromosuccinimide, and 4-bromobenzene (Aldrich Chem. Co.) and hydrogen peroxide (Duksan Sci. Co.) were used without further purification. Tetrahydrofuran (THF) was distilled over sodium and calcium hydride. Detailed.

The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were obtained using a Varian 200 (200 MHz) spectrometer. The photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (HITACHI, F-7000) and the ultraviolet-visible (UV-vis) spectra were obtained using UV-vis spectrophotometer (Shimadzu, UV-2501PC). Samples were dissolved in THF at a concentration of  $1.0 \times 10^{-4}$  M. Hexane and methanol were also used as the solvents for the PL measurement to confirm solvatochromic effect. Low temperature PL spectra were obtained at 77 K under liquid nitrogen. The differential scanning calorimetry (DSC) measurements were carried out using a Mettler DSC 822 at a heating rate of 10 °C/ min under nitrogen atmosphere. The mass spectrometry (MS) was performed using a JEOL, JMS-AX505WA spectrometer in FAB (fast atom bombardment) mode. Cyclic voltametry (CV) measurement was carried out in acetonitrile solution with tetrabutylammonium perchlorate at 0.1 M concentration. Organic materials were coated on indium tin oxide substrate and were immersed in electrolyte for analysis. Scan rate was 0.1 mV/s. Ferrocene was used as the reference material for the CV analysis. Elemental analysis of the materials was carried out using EA1110 (CE instrument). High performance liquid chromatography (HPLC) analysis of the synthesized materials was carried out using HPLC from Youngrin Instrument. A mixed eluent of acetonitrile:methanol (90:10) was used for the analysis.

#### 2.2. Synthesis

Detailed synthesis of the 3-(diphenylphosphoryl)-9-(4-(diphenylphosphoryl)phenyl)-9-carbazole (PPO21) was described in previous work [10].

#### 2.3. Synthesis of 9-(3-bromophenyl)-9H-carbazole (3)

A mixture of 9H-carbazole (4.0 g, 23.92 mmol), 1-bromo-3-iodobenzene (8.08 g, 28.70 mmol), Cu-powder (3.04 g, 47.84 mmol), potassium carbonate (13.20 g, 95.68 mmol) and dibenzo-18-crown-6 (0.63 g, 2.39 mmol) in dimethylformamide (DMF, 40 ml) was purged with argon and heated at reflux for 7 h. The mixture was quenched with H<sub>2</sub>O and extracted with dichloromethane. The organic fractions were dried with magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane to provided 5.67 g of title compound as white solid (m.p. 69– 70 °C; 71% yield).

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): (ppm) 8.15–8.12 (d, *J* = 6.0 Hz, 1H), 7.74–7.68 (m, 2H), 7.58–7.41 (m, 7H), 7.34–7.30 (m, 2H).

#### 2.4. Synthesis of 9-(2-bromophenyl)-9H-carbazole (5)

A mixture of 9H-carbazole (3.0 g, 17.94 mmol), 1-bromo-2-iodobenzene (10.15 g, 35.88 mmol), copper iodide (2.39 g, 12.55 mmol) and potassium carbonate (4.95 g, 35.88 mmol) in xylene (40 ml) was purged with argon and heated at reflux for 48 h. The mixture was quenched with H<sub>2</sub>O and extracted with dichloromethane. The organic fractions were dried with magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane to provide 2.5 g of title compound as white solid (m.p. 93–94 °C; 56% yield).

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): (ppm) 8.17–8.13 (d, *J* = 8.0 Hz, 1H), 7.90–7.68 (m, 1H), 7.57–7.29 (m, 8H), 7.08–7.02 (t, *J* = 6.0 Hz, 1H).

#### 2.5. Synthesis of 3-bromo-9-(3-bromophenyl)-9H-carbazole

Compound **3** (2.0 g, 6.20 mmol) was dissolved in dimethylformamide (DMF, 20 ml) under argon atmosphere. The reaction vessel was immersed in a ice bath until the temperature was about -20 °C and then *n*-bromosuccinimide (NBS, 1.32 g, 7.44 mmol) in DMF (5 ml) was added dropwise slowly into and stirred for 12 h. The mixture was allowed to gradually warm to room temperature overnight and then quenched with H<sub>2</sub>O followed by extraction with dichloromethane. The organic fractions were dried with magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane to provided 1.8 g of title compound as white solid (m.p. 187 °C; 80% yield).

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): (ppm) 8.45 (s, 1H), 8.25– 8.08 (t, *J* = 17.0 Hz, 3H), 7.86–7.66 (m, 3H), 7.55–7.31 (m, 5H).

# 2.6. Synthesis of 3-(diphenylphosphoryl)-9-(3-(diphenylphosphoryl)phenyl)-9H-carbazole (PPO25)

3-Bromo-9-(3-bromophenyl)-9H-carbazole (4.73 g, 11.79 mmol) was dissolved in tetrahydrofuran (THF, 50 ml) under argon atmosphere. The reaction vessel was immersed in a dry ice/acetone bath until the temperature was about -78 °C. To this solution 11.32 ml (28.30 mmol) of 2.5 M *n*-BuLi solution in hexane was added dropwise slowly and stirred for 3 h. Chlorodiphenylphosphine (5.22 ml, 28.30 mmol) was then added to the solution and stirred for 3 h in a dry ice/acetone bath. The mixture was allowed to gradually warm to room temperature overnight and then quenched with methanol, extracted with dichloromethane. The organic fractions were dried with magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane/dichloromethane (10:1) to provided 2.2 g of title compound as white solid (32% yield).

The white solid was dissolved in dichloromethane (40 ml) and hydrogen peroxide (8 ml) was stirred overnight at room temperature. The organic layer was separated and washed with dichloromethane and water. The extract was evaporated to dryness affording a white solid, which was further purified by column chromatography to yield 2.2 g of chemically pure PPO25 (purity 99.0% by HPLC).

Tg: 110 °C, <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): (ppm) 8.55–8.49 (d, *J* = 12.0 Hz, 1H), 8.08–8.05 (d, *J* = 6.0 Hz, 1H), 7.88–7.69 (m, 12H), 7.61–7.50 (m, 14H), 7.37–7.30 (t, *J* = 7.0 Hz, 3H) <sup>13</sup>C NMR (200 MHz, CDCl<sub>3</sub>): (ppm) 142.2, 140.8, 137.5, 137.1, 136.3, 134.3, 134.0, 132.6, 132.0, 131.4, 130.8, 130.9, 129.2, 129.0, 128.9, 128.2, 128.0, 127.9, 127.4, 126.1, 124.9, 123.9, 123.6, 123.0, 121.9, 121.4, 120.8, 120.2, 110.3, 109.2 MS (FAB) *m*/*z* 644 [(M + H)<sup>+</sup>] Anal. Calcd. for C<sub>42</sub>H<sub>31</sub>NO<sub>2</sub>P<sub>2</sub>: C, 78.37; H, 4.85; N, 2.18; O, 4.97. Found: C, 78.12; H, 4.81; N, 2.00; O, 5.04.

#### 2.7. Synthesis of 3-bromo-9-(2-bromophenyl)-9H-carbazole

Compound **5** (5.0 g, 15.51 mmol) was dissolved in dimethylformamide (DMF, 30 ml) under argon atmosphere. The reaction vessel was immersed in a ice bath until the temperature was about -20 °C and then *n*-bromosuccinimide (NBS, 3.0 g, 17.07 mmol) in DMF (15 ml) was added dropwise slowly into and stirred for 12 h. The mixture was allowed to gradually warm to room temperature overnight and then quenched with H<sub>2</sub>O followed by extraction with dichloromethane. The organic fractions were dried with magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane to provided 5.54 g of title compound as white solid (m.p. 190–194 °C; 89% yield).

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): (ppm) 8.26–8.22 (d, J = 8.0 Hz, 1H), 8.12–8.08 (d, J = 8.0 Hz, 1H), 7.88–7.68 (m, 2H), 7.55–7.30 (m, 5H), 7.07–7.01 (t, J = 6.0 Hz, 1H), 6.96–6.99 (t, J = 3 Hz, 1H).

## 2.8. Synthesis of 3-(diphenylphosphoryl)-9-(2-(diphenylphosphoryl)phenyl)-9H-carbazole (PPO26)

3-Bromo-9-(2-bromophenyl)-9H-carbazole (5.20 g, 12.96 mmol) was dissolved in tetrahydrofuran (THF, 50 ml) under argon atmosphere. The reaction vessel was immersed in a dry ice/acetone bath until the temperature was about -78 °C. To this solution 15.55 ml (38.89 mmol)

of 2.5 M *n*-BuLi solution in hexane was added dropwise slowly and stirred for 3 h. Chlorodiphenylphosphine (7.18 ml, 38.89 mmol) was then added to the solution and stirred for 3 h in a dry ice/acetone bath. The mixture was allowed to gradually warm to room temperature overnight and then quenched with methanol followed by extraction with dichloromethane. The organic fractions were dried with magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane/dichloromethane (10:1) to provided 2.6 g of title compound as white solid (33% yield).

The white solid was dissolved in dichloromethane (40 ml) and hydrogen peroxide (8 ml) was stirred overnight at room temperature. The organic layer was separated and washed with dichloromethane and water. The extract was evaporated to dryness affording a white solid, which was further purified by column chromatography to yield 2.8 g of chemically pure PPO26 (purity 99.1% by HPLC).

Tg: 110 °C, <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): (ppm) 8.33–8.27 (d, *J* = 12.0 Hz, 1H), 7.96–7.64 (m, 7H), 7.58–7.43 (m, 6H), 7.39–7.29 (m, 8H), 7.18–7.09 (t, *J* = 9.0 Hz, 3H), 7.01–6.94 (m, 6H) <sup>13</sup>C NMR (200 MHz, CDCl<sub>3</sub>): (ppm) 143.7, 142.6, 139.6, 136.4, 135.6, 134.6, 133.6, 132.9, 132.5, 132.1, 131.8, 130.4, 129.9, 129.2, 128.9, 128.1, 127.9, 127.5, 126.8, 123.0, 122.7, 121.2, 120.8, 120.5, 120.2, 119.6, 111.8, 110.8 MS (FAB) *m*/*z* 644 [(M + H)<sup>+</sup>] Anal. Calcd. for C<sub>42</sub>H<sub>31</sub>NO<sub>2</sub>P<sub>2</sub>: C, 78.37; H, 4.85; N, 2.18; O, 4.97. Found: C, 78.21: H, 4.84; N, 2.18; O, 4.99.

#### 2.9. Device fabrication

Α basic device configuration of indium tin 150 nm)/N,N'-diphenyl-N,N'-bis-[4-(phenyloxide(ITO, m-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine (DNTPD, 60 nm)/N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (NPB, 5 nm)/N,N'-dicarbazolyl-3,5-benzene (mCP, 10 nm)/PPO21 or PPO25 or PPO26: tris((3,5-difluoro-4-cyanophenyl)pyridine) iridium (FCNIr) (30 nm, 15%)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 15 nm)/LiF (1 nm)/ Al (200 nm) was used for the device fabrication. Hole only and electron only devices had device configurations of ITO/ DNTPD (60 nm)/NPB (5 nm)/mCP (10 nm)/host (30 nm)/Au and ITO/TSPO1 (10 nm)/host (30 nm)/TSPO1 (25 nm)/LiF (1 nm)/Al (100 nm), respectively. The evaporation rate of the organic materials was 0.1 nm/s and the deposition rate of the dopant was controlled according to the doping concentration of the dopant. Al was deposited at a deposition rate of 0.5 nm/s, while LiF deposition rate was 0.01 nm/s. The devices were encapsulated with a CaO getter and a glass rid after the device fabrication. The device performances of the blue PHOLEDs were measured with Keithley 2400 source measurement unit and CS1000 spectroradiometer.

#### 3. Results and discussion

Three host materials based on a phenylcarbazole core and a diphenylphosphine oxide substituent were synthesized. Three host materials had two diphenylphosphine oxide groups. One diphenylphosphine oxide group was attached to the phenyl unit of the phenylcarbazole, while the other diphenylphosphine oxide group was attached to the 3 position of the carbazole unit. The position of the diphenylphosphine oxide group attached to the phenyl unit was changed to study the effect of substitution position on the physical properties of the host material. All materials were synthesized by the reaction of the chlorodiphenylphosphine with brominated *N*-phenylcarbazole moiety followed by oxidation with hydrogen peroxide. Synthetic scheme of all materials is shown in Scheme 1. All materials were purified by column chromatography and a high purity level over 99% was obtained in all materials.

The energy level of the host material is critical to device performances of the PHOLED and is closely related with the molecular orbital distribution. Therefore, density functional theory (DFT) calculation of the host materials was carried out using a suite of Gaussian 03 program. The nonlocal density functional of Becke's 3-parameters employing Lee-Yang-Parr functional (B3LYP) with 6-31G\* basis sets was used for the calculation [25]. Fig. 1 shows the HOMO and the lowest unoccupied molecular orbital (LUMO) orbital distribution of host materials synthesized in this work. The HOMO was mostly distributed over the carbazole unit of the phenylcarbazole core, while the LUMO was dispersed over the phenyl unit of the phenylcarbazole core and diphenylphosphine oxide in all host materials [15]. The carbazole unit is an electron donating group and the HOMO was localized in the carbazole group. The diphenylphosphine oxide is a strong electron withdrawing group and the LUMO was dispersed over the phenyl and diphenylphosphine oxide groups. There was little difference of the molecular orbital distribution between the three materials. The calculated HOMO levels of the PPO21, PPO25 and



**Fig. 1.** Molecular simulation results of PPO21, PPO25 and PPO26. HOMO and LUMO orbital distribution is shown in this figure.

PPO26 were 5.56, 5.66 and 5.74 eV, while the LUMO levels were 1.12, 1.17 and 1.07 eV. Although the molecular orbital distribution of the three host materials was similar, the HOMO level was increased in the PPO26 with the diphenylphosphine oxide at ortho position. This indicates the



Scheme 1. Synthetic scheme of PPO21, PPO25 and PPO26.

reduction of the electron density in the carbazole group of the PPO26.

Photophysical properties of the host materials were analyzed with ultraviolet-visible (UV-vis) and photoluminescence (PL) measurements. UV-vis and PL spectra of the host materials are shown in Fig. 2. UV-vis absorption of the three host materials was similar and there was little shift of the UV-vis absorption peak. The main absorption of the three host materials is  $\pi - \pi$  transition of the phenylcarbazole core at 338 nm, resulting in similar absorption spectra. However, the PL spectra were different depending on the substitution position of the diphenylphosphine oxide. In particular, the PL spectrum of the PPO26 with the diphenylphosphine oxide at ortho position of the phenyl group was red-shifted and broadened compared with that of other host materials. The peak maximum of the PPO26 was 375 nm compared with 361 nm of the PPO25. The electron is partially transferred from the carbazole unit to the phosphine oxide unit, resulting in intramolecular charge transfer complex formation. The bandgap is reduced by the charge transfer complex formation, and the PL emission is red-shifted and broadened.

Solid PL spectra of the evaporated host materials are shown in Fig. 3. The solid PL spectra of the host materials were red-shifted and the full width at half maximum was also increased due to intermolecular interaction in solid state. In particular, the PPO26 with a phosphine oxide at ortho position showed two PL emission peaks at 367 and 450 nm. The PL emission peak at 367 nm is assigned to the PL emission of the phenylcarbazole core, while the PL emission at 450 nm is assigned to the emission of the intramolecular charge transfer complex. The intramolecular charge transfer emission was strong in the solid state by the solvent effect of polar PPO26 molecules. The UVvis absorption spectrum of the dopant material is also shown in Fig. 3. The PL emission of host materials was well overlapped with the UV-vis absorption of the FCNIr dopant, indicating efficient energy transfer from the host to dopant in solid state.

The intramolecular charge complex formation was confirmed from solution PL of host material using various solvents with different polarity. It is well known that strong solvatochromic effect is observed in the organic material



Fig. 2. UV-vis and solution PL spectra of PPO21, PPO25 and PPO26.



Fig. 3. Solid PL spectra of PPO21, PPO25 and PPO26. UV-vis spectrum of the FCNIr dopant was also added.

with charge transfer complex formation [26]. Fig. 4 shows the solution PL spectra of PPO25 and PPO26 at different solvents. Hexane, THF and methanol (MeOH) were used as the solvents. In the case of PPO25 with little intramolecular charge transfer complex formation, the PL emission was shifted only by 3–5 nm in highly polar MeOH solvent. However, the PL emission of PPO26 was red-shifted by more than 40 nm in highly polar solvent, proving the intramolecular charge transfer complex formation. Therefore, the solid PL emission of the PPO26 at long wavelength is originated from intramolecular charge transfer complex formation. The PPO26 is surrounded by higly polar PPO26 molecule and red-shifted PL emission of PPO26 by intramolecular charge transfer complex formation is observed.

The HOMO levels of three host materials were measured from the oxidation potential of the cyclic voltametry and the bandgap from UV-vis spectra. Energy levels of the host materials are summarized in Table 1. There was little difference of the HOMO and LUMO levels between the host materials. The HOMO was dispersed over the phenylcarbazole core in all host materials and similar HOMO levels were obtained. The LUMO was also distributed over the phenyl group substituted with diphenylphosphine oxide in all materials, resulting in similar LUMO levels. This can be further understood by analyzing the HOMO and LUMO distribution of 3-(diphenylphosphoryl)-9-phenyl-9H-carbazole (PPO1) without the diphenylphosphine oxide unit attached to the phenyl unit of the 9-phenylcarbazole [11]. The HOMO (6.16 eV) and LUMO (2.60 eV) of the PPO1 were localized in the carbazole unit with little dispersion over the phenyl unit. This indicates that the HOMO and LUMO of PPO1 are not greatly affected by substitution of electron withdrawing or donating moiety to the phenyl unit (less than 0.1 eV). Therefore, the substitution of the diphenylphosphine oxide group to the phenyl unit did not significantly change the HOMO and LUMO levels of host materials. In our previous work, the substitution of the diphenylphosphine oxide at the carbazole unit change the energy level by about 0.3 eV [11]. Therefore, the substitution of the diphenylphosphine oxide at the phenyl unit showed less significant effect on the energy level than the substitution of the diphenylphosphine oxide at the carbazole unit. Although the calculated HOMO level from



Fig. 4. Solution PL spectra of PPO25 (a) and PPO26 and (b) according to the polarity of solvent.

Table 1						
Physical	properties	of	PPO21,	PPO25	and	PPO26.

	Optical analysis				Electrical analysis		
	UV absorption (nm)	PL solution (nm)	PL solid (nm)	HOMO (eV)	LUMO (eV)	Bandgap (eV)	E <sub>T</sub> (eV)
PPO21	337	362	366	6.25	2.68	3.57	3.01
PPO25	338	364	367	6.25	2.70	3.55	2.99
PPO26	335	375	367 450	6.25	2.67	3.58	3.01

molecular simulation was shifted in the three host materials, experimental HOMO levels were the same in the three organic materials.

The triplet energy of the host materials was measured from low temperature PL emission peak and the triplet energy was 2.99–3.01 eV. All host materials showed a high triplet energy about 3.00 eV irrespective of the substitution position of the diphenylphosphine oxide. The triplet energy of the phenylcarbazole core was 3.01 eV and the diphenylphosphine oxide did not change the triplet energy of the phenylcarbazole core. As reported earlier, the diphenylphosphine oxide unit does not extend the conjugation of the core structure and did not reduce the triplet energy of the core [8]. Therefore, all host materials synthesized in this work can be effective as host materials for deep blue phosphorescent device. Deep blue PHOLEDs were fabricated using three host materials doped with deep blue emitting FCNIr dopant. Fig. 5 shows the current density–voltage–luminance curves of the deep blue PHOLEDs doped with FCNIr at a doping concentration of 20%. The current density was high in the PPO26 with the diphenylphosphine oxide at ortho position, while it was low in the PPO21 with the diphenylphosphine oxide at para position. The current density generally depends on the hole and electron density in the device. Therefore, hole and electron current density of three host materials was compared.

Current density-voltage curves of hole only and electron only devices of three host materials are shown in Fig. 6. The PPO26 showed the highest hole current density and lowest electron current density. The hole and electron current density depends on the energy barrier for charge



Fig. 5. Current density-voltage (a) and luminance-voltage and (b) curves of the deep blue PHOLEDs with the PPO21, PPO25 and PPO26.



Fig. 6. Current density-electric field curves of the hole only (a) and electron only and (b) devices with PPO21, PPO25 and PPO26.



**Fig. 7.** Quantum efficiency–luminance curves of the deep blue PHOLEDs with PPO21, PPO25 and PPO26 hosts.

injection and charge transport properties. Considering the HOMO level for hole injection, there should be no difference of the hole current density. Therefore, the increased hole current density of the PPO26 is due to improved hole transport properties of the PPO26. The origin for the improved hole transport properties of the PPO26 can be found in the intramolecular charge transfer complex formation in the PPO26. The carbazole unit donates electrons to the partially positive P atom in the phosphine oxide unit. This can give rise to weak p type doping effect in the carbazole unit, enhancing the hole transport properties of the PPO26. Similar increase of the hole current density by the weak p-type doping effect was reported in other work [27]. On the contrary, the electron donating effect of the carbazole to the P atom in the phosphine oxide has negative effect on the electron transport properties, leading to the low electron current density. The high hole and electron current density of the PPO25 compared with PPO21 may be due to small molecular size of the PPO25 for good hole and electron hopping. The HOMO and LUMO of the host materials were localized in the molecular structure and large molecule size hinders the charge transport through hopping.

Considering the hole and electron current density of the device, the high current density of the PPO26 device is due to high hole current density [28]. Both hole and electron current density of the PPO21 was lower than that of the PPO25, leading to low current density in the PPO21 device. The luminance followed the same relationship as the current density.

The quantum efficiency-luminance curves of the deep blue PHOLEDs are shown in Fig. 7. The PPO21 showed the highest maximum quantum efficiency of 20.4%, while the PPO25 and PPO26 showed the same maximum quantum efficiency of 17.1%. The maximum quantum efficiency of the PPO21 device is one of the best quantum efficiency value reported in the literature. Comparing the quantum efficiency at 1000 cd/m<sup>2</sup>, the PPO21 and PPO25 showed better quantum efficiency than PPO26. The quantum efficiency is generally affected by the charge balance in the emitting layer. As shown in the hole only and electron only device data, the PPO26 showed the highest hole current density and lowest electron current density. Therefore, the charge balance is worse than other host materials, which decreased the quantum efficiency of the PPO26 device. PPO25 was better than PPO21 in terms of efficiency roll-off. Balanced charge injection and balanced hole/electron density at low and high voltage improved the quantum efficiency at high luminance. Device data of the host materials are summarized in Table 2.

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Device performances of PPO21, PPO25 and PPO26 blue devices.

	Turn on voltage (V)	Driving voltage (V) <sup>a</sup>	Maximum quantum efficiency (%)	Quantum efficiency (%) <sup>a</sup>	Maximum power efficiency (lm/W)	Power efficiency (lm/W) <sup>a</sup>	Color coordinate <sup>a</sup>
PPO21	3.5	8.2	20.4 ± 1.7	11.9 ± 1.1	26.1 ± 2.4	6.6 ± 0.9	(0.14, 0.19)
PPO25	3.5	7.6	17.1 ± 1.3	$12.3 \pm 1.4$	21.2 ± 1.9	7.3 ± 1.0	(0.15, 0.19)
PPO26	3.5	7.2	17.1 ± 1.2	10.4 ± 1.3	20.6 ± 2.1	$6.4 \pm 0.8$	(0.15, 0.18)

<sup>a</sup> Data were measured at 1000 cd/m<sup>2</sup>.



Fig. 8. Electroluminescence spectra of the deep blue PHOLEDs with the PPO21, PPO25 and PPO26 hosts.

Electroluminescence (EL) spectra of the deep blue PHOLEDs are shown in Fig. 8. Three blue PHOLEDs showed similar EL spectra with a peak maximum at 454 nm. The color coordinate of the deep blue PHOLEDs was (0.14, 0.18) in all host materials. Therefore, high efficiency deep blue PHOLEDs with a *y* color coordinate less than 0.20 could be developed using the phenylcarbazole based phosphine oxide compounds.

#### 4. Conclusions

The photophysical properties and device performances of phenylcarbazole based phosphine oxide host materials were correlated with the substitution position of the phosphine oxide. The substitution at ortho position of the phenyl group induced an intramolecular charge transfer complex formation, while meta or para substitution did not significantly change the physical properties of the core structure. The ortho substitution enhanced the current density through intramolecular charge transfer, while the meta and para substitution enhanced the quantum efficiency of the deep blue PHOLEDs. A high quantum efficiency of 20.4% could be achieved using the high triplet energy host materials in deep blue PHOLEDs.

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