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Correlation of the substitution position of diphenylphosphine oxide on phenylcarbazole and device performances of blue phosphorescent organic light-emitting diodes[†]

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Two diphenylphosphine oxide modified phenylcarbazole host materials with substituents at 2,7 (**PPO27**) and 3,6 (**PPO36**) positions were synthesized and their device performances were correlated with the chemical structure of the host materials. Low driving voltage was obtained in the **PPO27** host with two diphenylphosphine oxides at 2,7 positions due to reduced band gap. The **PPO27** showed better performances in sky blue phosphorescent organic light-emitting diodes, while the PPO36 showed better performances in deep blue phosphorescent organic light-emitting diodes. A high quantum efficiency of 23.9% and power efficiency of 37.5 lm W⁻¹ were achieved in the blue device with **PPO27** host.

Introduction

The development of blue phosphorescent organic light-emitting diodes (PHOLEDs) is important because the power consumption of full color organic light emitting diodes is dominated by the quantum efficiency of the blue device.¹ Therefore, there have been many studies to improve the device performances of blue PHOLEDs by synthesizing new host and dopant materials.^{2–16} In particular, many host materials were synthesized and their device performances were investigated.^{8–30}

One of the best host materials to fabricate high efficiency blue PHOLEDs is a phosphine oxide type host material.¹³⁻²⁵ In general, a diphenylphosphine oxide unit was attached to the electron transport or hole transport type core. Fluorene,13,14 spirobifluorene,^{15,16} dibenzothiophene,¹⁷ dibenzofuran¹⁸ and phenylcarbazole¹⁹⁻²⁹ were representative core structures modified with the diphenylphosphine oxide. The diphenylphosphine oxide improved the electron transport properties of the host materials while keeping the triplet energy of the core structure. Therefore, bipolar type host materials could be developed by combining the hole transport type phenylcarbazole core with the diphenylphosphine oxide.¹⁹⁻²⁹ Several phenylcarbazole based phosphine oxide host materials were synthesized and their device performances were investigated. Phenylcarbazole compounds modified with one diphenylphosphine oxide or two diphenylphosphine oxide groups were reported and showed high quantum efficiency

in sky blue or deep blue PHOLEDs.^{19–23} In particular, the phenylcarbazole compounds with two diphenylphosphine oxide groups showed high quantum efficiency in deep blue PHO-LEDs.²⁰

The structure–property relationship of phenylcarbazole based compounds was theoretically studied in detail.²⁴ However, there was no experimental study about the effect of diphenylphosphine oxide position on the physical properties and device performances of phenylcarbazole compounds. Therefore, a more systematic study about the effect of substitution position of the diphenylphosphine oxide is required.

In this work, a phenylcarbazole type host material with two diphenylphosphine oxide groups at 2,7 positions of carbazole (**PPO27**) was synthesized and it was compared with a phenylcarbazole host modified with two diphenylphosphine oxide units at 3,6 positions (PPO36). It was demonstrated that the **PPO27** reduced the driving voltage and improved the quantum efficiency of blue PHOLEDs due to the reduced highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap and charge balance. A high quantum efficiency of 23.9% and power efficiency of 37.5 lm W⁻¹ were reported using the **PPO27**.

Experimental section

Synthesis

The synthetic route of the **PPO27** is shown in Scheme 1. The 2,7dibromo-9*H*-carbazole was synthesized according to the method reported earlier.³¹ The description of PPO36 is presented in our previous work.¹⁹

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Scheme 1 Synthetic scheme of PPO27.

Synthesis of 2,7-dibromo-9-phenyl-9*H*-carbazole (1)

A mixture of iodobenzene (2.1 g, 10.2 mmol), K_2CO_3 (1.42 g, 10.3 mmol) and ethylenediamine (0.17 ml, 2.5 mmol) in 15 ml of 1,4-dioxane was refluxed for 12 h after adding 2,7-dibromocarbazole in 10 ml of 1,4-dioxane drop wise. The mixture was quenched with H₂O and extracted with dichloromethane. The organic fractions were dried over MgSO₄, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane as the eluent to yield **1** (1.27 g, 60%) as a white solid (mp 182–183 °C).

¹H NMR (200 MHz, CDCl₃): (ppm) 7.97–7.93 (d, 3H), 7.68–7.48 (m, 5H), 7.42–7.38 (d, 3H).

Synthesis of 2,7-bis(diphenylphosphino)-9-phenyl-9*H*-carbazole (2)

Compound 1 (0.5 g, 1.2 mmol) was dissolved in 12 ml of tetrahydrofuran under argon atmosphere. The reaction vessel was immersed in a dry ice/acetone bath until the temperature went down to -78 °C. A 2.5 M *n*-BuLi solution (1.19 ml, 2.9 mmol) in hexane was added to the solution drop wise slowly and stirred for 3 h. Chlorodiphenylphosphine (0.55 ml, 2.9 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. The mixture was extracted with dichloromethane. The organic fractions were dried over MgSO₄, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane/dichloromethane (9 : 1) as the eluent to yield **2** (0.36 g, 50%) as a white solid. It was not purified and was used as the crude product for oxidation.

Synthesis of 2,7-bis(diphenylphosphoryl)-9-phenyl-9*H*-carbazole (PPO27)

Compound 2 was dissolved in a mixed solution of 5 ml dichloromethane and 1 ml of hydrogen peroxide and the solution was stirred overnight at room temperature. The mixture was extracted with dichloromethane after the reaction. The organic fractions were dried with MgSO₄, filtered, and the solvent was removed under reduced pressure. A white power (0.4 g) was obtained after drying. Purity: 99.4% (HPLC) mp 310–311 °C.

¹H NMR (200 MHz, CDCl₃): (ppm) 8.22–8.18 (d, 10H), 8.03– 7.96 (d, 10H), 7.71–7.61 (t, 6H), 7.53–7.40 (m, 5H). MS (FAB) m/z 644 [(M + H)⁺] ¹³C-NMR (200 MHz, CDCl₃): δ 141.46, 141.16, 136.02, 133.69, 132.52, 131.65, 130.77, 129.61, 129.22, 128.93, 128.15, 127.96, 127.47, 126.50, 125.14, 123.97, 123.78, 123.00, 122.81, 121.64, 121.35, 120.48, 120.19, 115.52, 114.36, 114.16. Anal. calcd. for $C_{42}H_{31}NO_2P_2$: C, 78.37; H, 4.85; N, 2.18. Found: C, 78.39; H, 4.89; N, 2.12.

Device preparation and measurements

A basic device configuration of indium tin oxide (ITO)/N, N'diphenvl-N,N'-bis-[4-(phenvl-m-tolyl-amino)-phenvl]-biphenvl-4,4'-diamine (DNTPD) (60 nm)/N,N'-di(1-naphthyl)-N, N'-diphenylbenzidine (NPB) (20 nm)/N,N'-dicarbazolyl-3,5benzene (mCP) (10 nm)/emitting layer/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 25 nm)/LiF/Al was used to evaluate the device performances of the blue PHOLEDs with the PPO27 and PPO36 host materials. Four different emitting layers were used to test the PPO27 and PPO36 host materials. Two blue with **PPO27** : iridium(III)bis(4,6-(di-fluolayers emitting rophenyl)-pyridinato-N,C')picolinate (FIrpic) and PPO36 : FIrpic were tested as the emitting layers in sky blue PHOLEDs, while two blue emitting layers with PPO27: tris((3,5-difluoro-4-cyanophenyl)pyridine)iridium (FCNIr) and PPO36 : FCNIr were evaluated as the emitting layers in deep blue PHOLEDs. The thickness of the emitting layers was 30 nm and the doping concentration was 10%. Electron only devices with a device structure of ITO/TSPO1 (5 nm)/PPO27 or PPO36 (30 nm)/TSPO1 (25 nm)/LiF/A1 and hole only devices with a device structure of ITO/DNTPD (60 nm)/NPB (20 nm)/mCP (10 nm)/PPO27 or PPO36 (30 nm)/DNTPD (5 nm)/Al were prepared to compare electron and hole transport properties of PPO27 and PPO36. All organic materials except dopant materials were deposited at 1 Å s⁻¹ evaporation rate. LiF was deposited at a rate of 0.1 Å s⁻¹ and Al was evaporated at a deposition rate of 5 Å s⁻¹. Devices were encapsulated with CaO getter and were sealed with a glass rid after device fabrication.

Energy levels of **PPO27** were measured with cyclic voltammetry and current density–voltage–luminance characteristics of the PHOLEDs were measured with a Keithley 2400 source measurement unit and CS1000 spectroradiometer. Detailed characterization method is described in the ESI[†].

Results and discussion

We reported phenylcarbazole host materials modified with diphenylphosphine oxide in our previous work.^{19,20} The aim of our previous work was to synthesize high triplet energy host materials with improved charge balance. The diphenylphosphine oxide unit was attached to the carbazole or phenyl unit of the phenylcarbazole. The substitution of the diphenylphosphine oxide group on the phenyl group was effective to improve the device performances of blue PHOLEDs. In addition to the substitution position of the diphenylphosphine oxide at the phenyl or carbazole units, the substitution position of the diphenylphosphine oxide on the carbazole may also affect the physical properties of host materials and device performances of blue PHOLEDs. Therefore, two different host materials with two diphenylphosphine oxide groups at 2,7 and 3,6 positions of carbazole were synthesized.

Two phosphine oxide modified phenylcarbazole compounds, **PPO27** and PPO36, were synthesized by the phosphorylation of

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the corresponding dibrominated phenylcarbazole intermediates. The 2,7-dibromo-9-phenylcarbazole intermediate was synthesized from 2,7-dibromo-9*H*-carbazole which was reported in other work^{31,32} and the synthesis of PPO36 was reported in our previous work.¹⁹ Various synthetic methods were reviewed in previous works and we followed the synthetic procedure presented in the work.³² Two materials were synthesized at a high purity over 99% after purification by column chromatography.

The substitution of the diphenylphosphine oxide at 2,7 and 3,6 positions has different effects on the HOMO/LUMO levels of the host materials because the molecular orbital distribution is different depending on the substitution position.²⁴ HOMO and LUMO distribution of PPO27 and PPO36 is shown in Fig. S1, (ESI[†]). The substitution at 2 and 7 positions does not have any great effect on the HOMO level, while the substitution at 3 and 6 positions affects the HOMO level of phenylcarbazole. The substitution of diphenylphosphine oxide at 2,7 positions may greatly change the LUMO level, while the substitution at 3,6 positions may have little effect on the LUMO level. Considering the HOMO and LUMO distributions of the phenylcarbazole, the HOMO is lowered in PPO36, while the LUMO is lowered in PPO27 by the substitution of electron withdrawing diphenylphosphine oxide group. As expected from the molecular orbital distribution, the simulated HOMO level of PPO36 (5.73 eV) was deeper than that of the PPO27 (5.64 eV), while the LUMO level of the PPO27 (1.36 eV) was deeper than that of the PPO36 (1.07 eV). Therefore, the HOMO-LUMO energy gap of the PPO27 (4.27 eV) was reduced compared with that of the PPO36 (4.66 eV). This result is consistent with the calculated data reported by Bredas's group.24

HOMO and LUMO levels of the PPO27 and PPO36 were measured from cyclic voltammetry (CV) and absorption edge of the ultraviolet-visible (UV-Vis) spectrum. CV data of PPO27 and PPO36 are shown in Fig. S2, (ESI[†]). The HOMO level of the PPO27 was 6.25 eV compared with 6.31 eV of PPO36. The HOMO level was shifted by 0.06 eV by the substitution of the diphenylphosphine oxide at 3,6 positions. The LUMO level was calculated from the HOMO level and optical band gap from UV-Vis absorption spectra and the LUMO levels of PPO27 and PPO36 were 3.00 eV and 2.77 eV respectively. The LUMO level of the PPO27 was shifted by 0.23 eV by the electron withdrawing phosphine oxide group. As shown in the molecular orbital distribution, the LUMO was dispersed over 2,7 positions of the phenylcarbazole. Therefore, the substitution of the strong electron withdrawing diphenylphosphine oxide at 2,7 positions shifted the LUMO level significantly. In addition, the LUMO was extended to the diphenylphosphine oxide group due to extended conjugation through 2,7 positions. The shift of the LUMO level also led to the decrease of the HOMO-LUMO gap from 3.54 eV of PPO36 to 3.25 eV of PPO27.

Photophysical properties of the **PPO27** and **PPO36** were compared and they are shown in Fig. 1. UV-Vis, photoluminescence (PL) and low temperature PL spectra of host materials were compared. The UV-Vis spectrum was red-shifted in the **PPO27** compared with that of the PPO36 due to the reduced HOMO–LUMO gap. The PL spectra were also shifted by 26 nm due to the reduced HOMO–LUMO gap of **PPO27**. The maximum peak of PL emission of **PPO27** was 392 nm compared with 366 nm of PPO36. The triplet energy of the



Fig. 1 UV-Vis, solution PL, solid PL and low temperature PL spectra of **PPO27** and PPO36.

PPO27 and PPO36 can also be calculated from the emission peak of low temperature PL spectra and it was 2.81 eV and 3.01 eV, respectively. The reduced triplet energy of the **PPO27** is due to the reduction of the HOMO–LUMO gap. Although the triplet energy of the **PPO27** was lowered by substitution at 2,7 positions, the triplet energy of the **PPO27** was higher than those of blue emitting dopants such as FCNIr and FIrpic. The triplet energies of the FCNIr and FIrpic were 2.75 eV and 2.65 eV, respectively.

UV-Vis absorption of blue dopants and PL emission of blue host materials were plotted in Fig. 2 to confirm the energy transfer from host materials to dopant materials. The FCNIr showed absorption below 430 nm, which was exactly overlapped with the singlet and triplet emissions of PPO36. In the case of **PPO27**, the singlet emission was overlapped with the absorption of FCNIr, but the triplet emission was little overlapped due to decreased triplet energy. The FIrpic showed strong absorption below 460 nm, which was well overlapped with the emission of **PPO27** and PPO36. Therefore, it can be expected that energy transfer from **PPO27** and PPO36 hosts to FIrpic is effective, but the energy transfer from **PPO27** to FCNIr may not be so effective as that from PPO36 to FCNIr.

The **PPO27** and PPO36 showed different HOMO/LUMO levels and molecular orbital distributions, which may affect the hole and electron transport properties of **PPO27** and PPO36. Therefore, hole only and electron only devices of **PPO27** and PPO36 were fabricated to compare the hole and electron density in the **PPO27** and PPO36. Hole current density–voltage and electron current density–voltage curves of **PPO27** and PPO36



Fig. 2 UV-Vis absorption spectra of FCNIr and FIrpic dopants compared with PL emission spectra of **PPO27** and **PPO36**.





Fig. 3 Current density-voltage curves of hole only and electron only devices of **PPO27** and PPO36.

are shown in Fig. 3. Both the hole current density and electron current density were high in the PPO27 device compared with those of the PPO36 device. This indicates that the PPO27 is better than PPO36 in terms of hole and electron injection. The hole and electron current densities are determined by the energy barrier for charge injection and charge transport properties. Comparing the HOMO levels, the HOMO level of PPO27 (6.25 eV) is more suitable for hole injection than that of PPO36 (6.31 eV). Therefore, the PPO27 can effectively inject holes from a hole transport layer. In addition, the HOMO orbital distribution of the **PPO27** is more suitable for hole transport. As shown in HOMO distribution of phenylcarbazole, the substitution of diphenylphosphine oxide at 3,6 positions disturbs the hole transport due to the electron withdrawing character of the diphenylphosphine oxide. However, the HOMO of phenylcarbazole is maintained constant irrespective of the diphenylphosphine oxide substitution at 2,7 positions. Therefore, the **PPO27** is better than PPO36 for hole injection and transport. Hole and electron mobility of the PPO27 and PPO36 was measured to confirm the charge transport properties of the host materials. The hole mobilities of PPO27 and PPO36 were 8 \times 10^{-5} cm² V⁻¹ s⁻¹ and 2 × 10⁻⁵ cm² V⁻¹ s⁻¹, which confirm that **PPO27** is better than PPO36 in terms of hole mobility.

Similarly, the electron density of the PPO27 was higher than that of the PPO36. Although the LUMO level of PPO27 was lower than that of PPO36 by 0.20 eV, there was no energy barrier for electron injection from TSPO1 to PPO27 and PPO36. Therefore, the high electron current density of the PPO27 device is due to improved electron transport properties of PPO27, which are related with the LUMO distribution of the PPO27. The LUMO of **PPO27** is dispersed by the electron withdrawing diphenylphosphine oxide, while the LUMO of PPO36 is not extensively dispersed by the diphenylphosphine oxide because the node of the LUMO was at 3,6 positions. Therefore, PPO27 can be better than PPO36 in terms of electron transport. The electron mobility of the **PPO27** was 7×10^{-6} cm² V⁻¹ s⁻¹, which was higher than that of PPO36 with a electron mobility of 2 \times 10^{-6} cm² V⁻¹ s⁻¹. Therefore, the hole and electron current densities of PPO27 were higher than that of PPO36.

As the **PPO27** and PPO36 had high triplet energy for energy transfer to blue phosphorescent dopants, **PPO27** and PPO36 based blue PHOLEDs doped with FIrpic and FCNIr were fabricated. The doping concentration of the blue phosphorescent dopant was optimized at 15%. Fig. 4 shows current density–voltage–luminance curves of the **PPO27** and **PPO36** blue



Fig. 4 Current density–voltage–luminance curves of **PPO27** and **PPO36** blue devices doped with FIrpic and FCNIr.

PHOLEDs. The current density of the **PPO27** blue PHOLED was much higher that of PPO36 blue PHOLED over all voltage ranges investigated. The high current density of the **PPO27** device is due to high hole and electron current densities as explained in Fig. 3. In the case of the FIrpic devices, the turn-on voltage of the **PPO27** device was 3.0 V compared with 3.5 V of PPO36 device and the driving voltage at 1000 cd m⁻² was lowered by 2.5 V. The driving voltage at 1000 cd m⁻² was 8.1 V in the PPO36 device, while it was 5.6 V in the **PPO27** device.

The quantum efficiency–luminance and power efficiency– luminance curves of **PPO27** and **PPO36** devices are shown in Fig. 5. In the case of FIrpic devices, the **PPO27** device showed much higher quantum efficiency and power efficiency than **PPO36** device. The **PPO27** improved both hole and electron current densities, and further improved charge balance in the emitting layer. The **PPO27** had a high triplet energy of 2.81 eV for efficient energy transfer to FIrpic and balanced charge injection through 2,7 substitution of diphenylphosphine oxide



Fig. 5 Quantum efficiency–luminance (a) and power efficiency–luminance (b) curves of **PPO27** and PPO36 blue devices doped with FIrpic and FCNIr.

 Table 1
 Device performances of blue PHOLEDs fabricated in this work

Emitting layer	Quantum efficiency (%)		Power efficiency/lm W ⁻¹	
	Max.	$1000 \text{ cd } \text{m}^{-2}$	Max.	1000 cd m ⁻¹
PPO27 : FIrpic PPO27 : FCNIr PPO36 : FIrpic PPO36 : FCNIr	23.9 16.2 16.4 19.8	20.3 13.5 14.1 14.9	37.5 15.1 23.2 19.9	23.0 8.7 10.5 7.0

groups. The maximum quantum efficiency of the PPO27 device was 23.9% and the quantum efficiency at 1000 cd m^{-2} was 20.3%, while the maximum quantum efficiency and quantum efficiency at 1000 cd m⁻² of PPO36 device were 16.4% and 14.1%, respectively. The quantum efficiency was improved by more than 50% by substituting the diphenylphosphine oxide at 2,7 positions instead of 3.6 positions. In addition to the quantum efficiency. the power efficiency was also significantly improved. The maximum power efficiency and power efficiency at 1000 cd m⁻² of the **PPO27** device were $37.5 \text{ Im } \text{W}^{-1}$ and $23.0 \text{ Im } \text{W}^{-1}$, while the maximum power efficiency and power efficiency at 1000 cd m⁻² of the PPO36 device were 23.2 lm W⁻¹ and 10.4 lm W⁻¹, respectively. In particular, the power efficiency at 1000 cd m⁻² was more than doubled by using the **PPO27** instead of PPO36. The power efficiency is generally determined by the driving voltage and quantum efficiency. Therefore, the high power efficiency of the PPO27 device is due to lowered driving voltage and improved quantum efficiency. The driving voltage was lowered by 2.5 V and the quantum efficiency was enhanced by 60% in the PPO27 device. This quantum efficiency value was high although it was lower than that of the best efficiency values in sky blue PHOLEDs.^{33,34} The best quantum efficiency of sky blue PHO-LEDs was 26%. The device performances of the PPO27 and PPO36 blue PHOLEDs are summarized in Table 1. In addition, the quantum efficiency of the PPO27: FIrpic device was compared with other data reported in FIrpic based blue PHO-LEDs with phenylcarbazole and diphenylphosphine oxide groups (Table 2).

In the case of the FCNIr devices, the PPO36 showed better quantum efficiency than **PPO27** although the power efficiency was high in **PPO27** device owing to a low driving voltage. The high quantum efficiency of the PPO36 device compared with that of **PPO27** device may be related with the energy transfer from host to dopant material. In the FIrpic devices, the triplet energy of the host materials was higher that that of FIrpic (2.65 eV), resulting in efficient energy transfer from host materials to dopant. However, the triplet energy of the **PPO27** (2.81 eV) was



Fig. 6 PL spectra of **PPO27** and **PPO36** films doped with FIrpic and FCNIr. The films were excited at 400 nm.

higher than that of the FCNIr (2.75 eV) by only 0.06 eV, which may induce reverse energy transfer from FCNIr to **PPO27**. The reverse energy transfer degrades the quantum efficiency of the device because of triplet exciton quenching by the host material. The triplet energy of the PPO36 (3.01 eV) is high enough and no reverse energy transfer can be induced.

To confirm the reverse energy transfer in the **PPO27** : FCNIr emitting layer, PL measurement of the PPO27 : FCNIr and PPO36: FCNIr films was carried out. PL spectra of PPO27 : FIrpic and PPO36 : FIrpic were also obtained for comparison. Fig. 6 shows the PL spectra of the four different films. Excitation wavelength of the film was set as 400 nm, which excites only dopant materials without any excitation of the host materials. There was little difference of the PL spectra in the FIrpic doped **PPO27** and PPO36. As there was no energy transfer from FIrpic to host materials, identical FIrpic spectra were observed in both films. However, the PL spectra of the FCNIr doped PPO27 and PPO36 films were different. They showed same emission spectra at long wavelength, but the emission between 430 nm and 500 nm were suppressed in FCNIr doped PPO27 film. Assuming that there is no energy transfer from FCNIr dopant to the PPO27 or PPO36 host, there should be no difference of PL spectra. Therefore, the reduction of relative PL intensity in the PPO27 : FCNIr film indicates the energy transfer from FCNIr to the PPO27. In particular, the vibrational peaks at short wavelength were reduced due to high energy of the short wavelength emission. Therefore, it can be proved that the low quantum efficiency of the FCNIr doped **PPO27** device is due to reverse energy transfer from FCNIr to PPO27. Similar PL spectra were observed when the FCNIr doped film was excited at 330 nm light source. PPO27 and PPO36 are excited at 330 nm and the PL spectra show the light emission by energy transfer from host to dopant materials. The same PL spectra were obtained irrespective of the excitation

Table 2 Device performances of blue PHOLEDs with phenylcarbazole based host material doped with FIrpic

Host material	Quantum efficiency (%)	References	
3.6-Bis(diphenylphosphoryl)-9-ethylcarbazole	$\sim 5\%$	23	
N-(4-Diphenylphosphoryl phenyl)carbazole (MPO12)	9.1%	25	
4,4',4"-Tri(N-carbazolyl)triphenylphosphine oxide	$\sim \! 16.0\%$	26	
2,7-Bis(diphenylphosphine oxide)-9-(9-phenylcarbazol-3-yl)-9-phenylfluorene	14.8%	27	
2,7-Bis(diphenylphosphoryl)-9-phenyl-9H-carbazole	23.9%	This work	



Fig. 7 Electroluminescence spectra of **PPO27** and **PPO36** blue devices doped with FIrpic and FCNIr.

wavelength and this is also due to reverse energy transfer from FCNIr to **PPO27**. Energy transfer from **PPO27** to FCNIr is induced at 330 nm excitation wavelength, but the reverse energy transfer follows, leading to the reduction of the emission intensity at short wavelength.

Electroluminescence (EL) spectra of the PPO27 and PPO36 devices are shown in Fig. 7. Both PPO27 and PPO36 showed strong emission peaks originated from the FIrpic and FCNIr dopant materials. However, the EL spectra were a little different from PL spectra and first vibrational peak was intensified in the PPO27. The strong intensity of the vibration peak in PPO27 device is due to the optical effect caused by the recombination zone shift. In the FCNIr device case, the reduction of the short wavelength emission was also observed due to reverse energy transfer. Full width at half maximum (FWHM) of the blue PHOLEDs was between 52 nm and 54 nm except for **PPO27** : FCNIr. This indicates that there was no reverse energy transfer in the **PPO27** : FIrpic, PPO36 : FIrpic and PPO36: FCNIr devices. However, the FWHM of the **PPO27** : FCNIr was 61 nm, which was higher than that of other devices. This is due to the reverse energy transfer causing the reduction of the deep blue emission.

The energy transfer of the **PPO27** based device was further studied by absolute PL quantum efficiency measurement and transient PL experiment. Absolute quantum efficiency of the PPO36 : FIrpic and **PPO27** : FIrpic was 87.5% and 88.5%, while that of the PPO36 : FCNIr and **PPO27** : FCNIr was 85.4% and 79.1%. The PL quantum efficiency of the **PPO27** : FCNIr was reduced because of the reverse energy transfer from FCNIr to



Fig. 8 Transient PL decay of **PPO27** and **PPO36** solid film doped with FIrpic and FCNIr.

PPO27. Fig. 8 shows the transient EL spectra of **PPO27** and PPO36 solid films doped with FIrpic and FCNIr. The monoexponential decay curve was observed and the excited state lifetime of the FIrpic doped solid film was 1.21 μ s and 1.29 μ s for **PPO27** and PPO36, respectively. Similar excited state lifetime for phosphorescence emission was observed. There was little effect of the host on the lifetime of the FIrpic device. The PPO36 : FCNIr film also exhibited mono-exponential decay curve and the excited state lifetime was 1.72 μ s, which was a little longer than that of the PPO36 : FIrpic. In the case of **PPO27** : FCNIr film, weak double exponential decay behavior was observed in the transient PL decay curve. The lifetime for the first decay and the second decay was 1.19 μ s and 7.18 μ s. The double exponential decay of the transient PL indicates the reverse energy transfer process in the **PPO27** : FCNIr.

Conclusions

The substitution of diphenylphosphine oxide at 2,7 positions of carbazole unit improved hole and electron injection into the emitting layer and reduced the driving voltage of blue PHO-LEDs. In particular, the **PPO27** with substituents at 2,7 positions greatly improved the power efficiency of FIrpic doped sky blue PHOLEDs due to high quantum efficiency and low driving voltage. A high quantum efficiency of 23.9% and power efficiency of 37.5 lm W⁻¹ were achieved in the blue PHOLED with FIrpic doped **PPO27** host. However, the substitution at 3,6 positions (PPO36) was better than 2,7 substitution in the FCNIr doped deep blue PHOLEDs because of reverse energy transfer in the **PPO27** device.

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