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High-Efficiency Deep-Blue-Phosphorescent Organic Light-Emitting Diodes Using a Phosphine Oxide and a Phosphine Sulfide High-Triplet-Energy Host Material with Bipolar Charge-Transport Properties

By Soon Ok Jeon, Kyoung Soo Yook, Chul Woong Joo, and Jun Yeob Lee*

Blue-phosphorescent organic light-emitting diodes (PHOLEDs) have been developed for more than 10 years towards use in active-matrix-type organic light-emitting diodes. There has been much improvement in quantum efficiency, lifetime, and color purity although the device performances of the blue PHOLEDs are not yet good enough for practical applications.

Most research into blue PHOLEDs was focused on the development of new host and dopant materials. $^{\left[1-14\right] }$ The best-known host material in the blue PHOLEDs is N,N-dicarbazolyl-3,5-benzene (mCP).^[1] It has good hole-transport properties due to a carbazole unit in the backbone structure and a wide triplet bandgap of 2.90 eV for efficient energy transfer. However, its electron injection and transport properties are poor because of the high energy of the lowest unoccupied molecular orbital (LUMO) of 2.4 eV. Silicone-based wide-triplet-bandgap host materials were also developed^[2–5] and tetraaryl-based silane materials have been used as host materials in blue PHOLEDs.^[2,3] However, the energy of the highest occupied molecular orbital (HOMO) of the silane-based host materials is around 7.0 eV, which is not suitable for hole injection. Therefore, it was difficult to balance holes and electrons in the light-emitting layer. To overcome the poor hole injection in the silane-based host materials, silane compounds with a carbazole moiety in the molecular structure were evaluated as triplet host materials in blue PHOLEDs.^[4,5] However, the carbazole-based host materials showed strong hole-transport properties and bipolar transport behavior was not observed. In addition, phosphine oxide-type host materials were synthesized, but only sky-blue PHOLEDs were reported due to the low triplet energy.^[6,7] Our group also reported phosphine oxide-type host materials with a carbazole moiety in the backbone structure and high efficiency could be obtained.^[14]

Although several classes of host materials have been synthesized, no host materials could show a theoretical maximum quantum efficiency in the deep-blue PHOLED with Commission International De L'Eclairage (CIE) color coordinate (x + y) values below 0.30. In this work, we synthesized bipolar-type high-triplet-energy host materials with a carbazole

 [*] Prof. J. Y. Lee, S. O. Jeon, K. S. Yook, C. W. Joo Department of Polymer Science and Engineering Dankook University
 126, Jukjeon-dong, Suji-gu, Yongin, Gyeonggi, 448-701 (Korea)
 E-mail: leej17@dankook.ac.kr

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core structure. Phosphine oxide (PPO21) and phosphine sulfide (PPS21) host materials with the carbazole core structure were synthesized and evaluated as host materials in the deep-blue PHOLEDs. A theoretical maximum quantum efficiency over 19% with a deep-blue CIE coordinate of (0.14,0.16) was demonstrated in the deep-blue PHOLEDs using the high-triplet-energy host materials for the first time.

The host materials synthesized in this work have a 9-phenylcarbazole core structure with two phosphine oxide or phosphine sulfide units. One diphenylphosphine oxide or sulfide unit was attached to the 3-position of the carbazole unit to control the HOMO level and the charge transport properties. The other diphenylphosphine oxide or sulfide unit was connected to the phenyl group of the 9-phenylcarbazole to manage the electronn-transport properties.

The host materials were synthesized by the coupling reaction of the chlorodiphenylphosphine with 3-bromo-9-(4-bromophenyl)carbazole using *n*-butyllithium followed by oxidation and sulfonation (Scheme 1). The product was purified by a column chromatography and it was confirmed with ¹H NMR spectroscopy, differential scanning calorimetry (DSC), high performance liquid chromatography (HPLC) and mass spectrometry (MS). The purity of the host materials was over 99% from HPLC. Physical properties of the host materials are summarized in Table 1..

The two high-triplet-energy host materials showed high glass-transition temperature (T_g) above 110 °C due to the two rigid diphenylphosphine oxide or sulfide groups. The significantly higher T_g of the PPS21 compared to PPO21 is due to large atom size of the sulfur. The two diphenylphosphine oxide or sulfide units also stabilized the amorphous morphology of the host materials, and a smooth surface roughness less than 1 nm was obtained from the evaporated film. The surface morphology of the evaporated films was kept stable even after thermal treatment at 80 °C for 1 h because of the rigid molecular structure and corresponding high T_g .

The HOMO and LUMO levels of the host materials were measured using cyclic voltametry (CV), and they are summarized in Table 1. The HOMO/LUMO levels of the PPO21 and PPS21 are mainly determined by the carbazole backbone structure, and the diphenylphosphine oxide or sulfide groups shift the HOMO/LUMO levels through the control of the electron density in the carbazole core. The HOMO level of the PPO21 was 6.25 eV, which corresponds to a change of 0.37 eV compared with that of the phenylcarbazole moiety without any substituent, 5.88 eV.^[15] The LUMO level (2.68 eV) of the PPO21 was also shifted by 0.30 eV by the diphenylphosphine oxide unit. The electron withdrawing

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Scheme 1. Synthetic scheme of the PPO21 and PPS21.

character of the diphenylphosphine oxide shifted the HOMO/ LUMO levels far away from the vacuum level. This also indicates that the electron-transport properties of the PPO21 can be improved compared with those of the carbazole because of the highly polar and electron-withdrawing phosphine oxide group. Compared with the PPO21, the HOMO/LUMO-level shift in PPS21 was less significant and HOMO/LUMO levels of 6.14 eV/ 2.58 eV were obtained. The difference of the energy-level shift depending on the pendant group attached to the carbazole core structure can be explained by the polarity of the phosphine oxide and phosphine sulfide groups. It was reported that the polarity of the P = X unit is increased in an order of O > S.^[16] Therefore, the highly polar $P\!=\!O$ group withdraws more electrons from the carbazole core, resulting in the large energy-level shift. The bandgap was not affected by the substituent of the carbazole core. The triplet energy of the two materials was almost the same because the triplet energy is determined by the carbazole core (3.02 eV). The diphenylphosphine-based groups did not change the triplet energy level of the carbazole core as the conjugation of the carbazole core could not be extended further. The triplet energy of the host materials was wider than that of the tris[(3,5-difluoro-4-cyanophenyl)pyridine] iridium (FCNIr) dopant with a triplet bandgap of 2.80 eV,^[8,9] and efficient energy transfer from the host materials to the FCNIr is expected.

Molecular simulation of the PPO21 and PPS21 was carried out to study the HOMO/LUMO levels of the host materials in molecular scale and is shown in Figure 1. The HOMO of the PPO21 and PPS21 was localized in the carbazole backbone structure and the phosphine oxide and sulfide unit linked to the carbazole unit also contributed to the HOMO. Compared with the HOMO localized in the carbazole core, the LUMO was mostly distributed over the diphenylphosphine oxide- and sulfide-substituted phenyl unit attached to the carbazole core structure. This indicates that the HOMO level of the PPO21 and PPS21 is mainly determined by the carbazole backbone structure, while the LUMO level is mostly affected by the diphenylphosphine oxide- or sulfide-substituted phenyl group attached to the carbazole core. In other words, the diphenylphosphine oxide or sulfide group linked to the carbazole unit controls the HOMO energy level, while the second diphenylphosphine oxide or sulfide group connected to the phenyl group influences the LUMO energy level of PPO21. In addition, the LUMO distribution in the diphenylphosphine oxide- or

sulfide-substituted phenyl group implies that the electrontransport properties of the PPO21 and PPS21 can be improved compared with those of the carbazole because of the highly polar and electron-withdrawing phosphine oxide or sulfide group. In particular, the LUMO mostly depends on the diphenylphospine oxide- or sulfide-substituted phenyl group, without significant contribution from the carbazole group and its strong holetransport properties, leading to an appropriate LUMO energy for electron injection. It is expected that the PPO21 shows better electron-transport properties than the PPS21 because the LUMO orbital distribution is localized in the diphenylphosphine oxide-substituted phenyl group.

The host materials showed a main absorption peak of the carbazole core at around 295 nm and 338 nm. As the diphenylphosphine oxide and diphenylphosphine sulfide did not affect the ultraviolet-visible (UV–vis) absorption of the host materials, similar UV–vis absorption peaks were observed. A photoluminescence (PL) emission peak of the host materials was observed between 361 and 367 nm from emission of the carbazole core.^[15] The PL emission peak of the host materials was well overlapped with the metal-to-ligand charge-transfer absorption peak of the FCNIr around 420 nm, indicating efficient energy transfer from the host materials to the FCNIr.

The phosphine oxide and phosphine sulfid-type materials are suitable host materials for deep-blue PHOLEDs due to their wide triplet bandgap over 3.00 eV and their properties as host materials were evaluated.

Table	1.	Physical	properties	of the	PPO21	and	PPS21.
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	Optical Analysis		Thermal Analysis		Electrical Analysis				
	Absortion [nm]	Emission [nm]	T _g [°C]	T _m [a] [°C]	HOMO [eV]	LUMO [eV]	Bandgap [eV]	<i>E</i> _⊤ [b] [eV]	
PPO21	294, 338	361	111	_	6.25	2.68	3.57	3.01	
PPS21	296, 338	366	120	254	6.14	2.58	3.56	3.00	

[a] melting temperature.[b] triplet energy.





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Figure 1. Molecular-simulation results of PPO21 and PPS21. HOMO and LUMO distributions are shown in this figure.

A basic device configuration was: indium tin oxide (ITO; 150 nm)/N,N'-diphenyl-N,N'-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine (DNTPD; 60 nm)/N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (NPB; 10 nm)/N,N'-dicarbazolyl-3,5-benzene (mCP; 20nm)/host:FCNIr (30 nm; 15%)/4,7-diphenyl-1,10-phenanthroline (Bphen; 25 nm)/LiF (1 nm)/Al (200 nm). The doping concentration of the FCNIr was 15% and two host materials were used as the high-triplet-energy host in the emitting layer.

Hole-only and electron-only devices of the PPO21 and PPS21 were fabricated to compare the hole and electron density in the emitting layer. Device structures of the hole-only and electron-only devices were ITO/DNTPD (60 nm)/NPB (10 nm)/mCP

(20 nm)/host (30 nm)/Bphen (25 nm)/DNTPD (10 nm)/Al and ITO/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (10 nm)/DNTPD (60 nm)/ NPB (10 nm)/mCP (20 nm)/host (30 nm)/ Bphen (25 nm)/LiF/Al, respectively. Figure 2 shows the current-density-voltage curves of the PPO21 and PPS21 hole- and electron-only devices. The hole-current density was high in the PPS21, while the electron-current density was high in the PPO21. This indicates that the PPO21 shows better performance than PPS21 in terms of electron injection, while PPS21 performs better than the PPO21 in terms of hole injection. The high hole-current density in PPS21 can be explained by the energy of the

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HOMO level and the hole mobility of PPS21 compared with those of the PPO21. The HOMO energy level of the PPS21 is 0.11 eV higher than that of the PPO21 and hole mobility of the PPS21 (3×10^{-5} cm² V⁻¹ s⁻¹) is higher than that of the PPO21 (9×10^{-6} cm² V⁻¹ s⁻¹), leading to a better hole injection. Similarly, the electron-current density was high in the PPO21 due to the appropriate LUMO level for better electron injection and high electron mobility. The electron mobility of the PPO21 was 3×10^{-6} cm² V⁻¹ s⁻¹ compared with 5×10^{-7} cm² V⁻¹ s⁻¹ of the PPS21. There was no large difference of the hole- and electron-current density in the PPO21, but the hole-current density was much higher than the electron-current density in PPS21. Therefore, it can be expected that holes and electrons can be balanced in the PPO21. These results indicate that the PPO21 shows bipolar charge-transport properties.

The device performances of the PPO21 and PPS21 blue PHOLEDs are shown in Figure 3. The current density was high in the PPS21 device, while the luminance was high in the PPO21 device. Although the current density was high in the PPS21 device, due to efficient hole injection, the poor electron injection in the PPS21 device decreased the luminance of the PPS21 device. Therefore, the quantum efficiency, which is determined by the current density and the luminance was high in the PPO21 device, while the quantum efficiency was relatively low in the PPS21 device. The holes and electrons were balanced in the PPO21 device, while holes dominated the electrons in the PPS21 device, as shown in Figure 2. The quantum efficiency of the PPO21 device was over 50% higher than that of the PPS21 device. A maximum quantum efficiency of 19.2% was achieved in the PPO21 device while the quantum efficiency of the PPO21 device was 15.2% at 100 cd m⁻² and 12.1% at 1000 cd m⁻² with a CIE color coordinate of (0.14,0.16). The quantum efficiency of the PPO21 device was higher than the theoretical maximum quantum efficiency 19% and this value is better than any other data reported in the literature.^[8,10,11,14] The problem of the rapid efficiency roll-off in the deep-blue device was greatly improved in the deep-blue PHOLEDs with the PPO21 host, and the high quantum efficiency was achieved even at high luminance. The maximum current efficiency was 22.5 cd A^{-1} and the maximum power efficiency was $19 \text{ lm } \text{W}^{-1}$ in the PPO21 device. The current efficiency and power efficiency of the PPO21 device were 18.1 cd A^{-1} and 9.0 lm W^{-1} at 100 cd m⁻². The balanced charge injection originated from the HOMO/LUMO level management, using the electron-withdrawing phosphine oxide group in



Figure 2. Current-density-voltage curves of the hole only (a) and electron only (b) devices of PPO21 and PPS21.

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Figure 3. Current-density–luminance–voltage (a), quantum-efficiency–luminance (b), and electroluminescence (c) curves of the deep-blue PHOLEDs with PPO21 and PPS21 host materials.

PPO21, and resulted in the high quantum efficiency. Therefore, the PPO21 is a promising host material for the deep-blue PHOLEDs. However, the lifetime of the PPO21 device was only a few hours at 100 cd m⁻² and further development of the charge-transport materials as well as the host and dopant materials may increase the lifetime of the deep-blue PHOLEDs. Further optimization of the PPO21 deep-blue devices will follow to enhance the lifetime of the device using various high-triplet-energy charge transport materials.

Electroluminescence spectra of the PPO21 and PPS21 deep-blue PHOLEDs are also shown in Figure 3. PPO21 and PPS21 devices showed a strong peak at 452 nm assigned to FCNIr emission in addition to a vibrational peak at 482 nm. The vibration peak at 482 nm was suppressed in the PPO21 device and it showed a CIE value of (0.14,0.16). In PPS21 device, the strong vibrational peak at 482 nm degraded the color performances of

the deep-blue PHOLEDs. The vibrational peak was intensified in the PPS21 device because of the difference of the recombination zone.^[17] The recombination zone is shifted from the holetransport-layer side to the electron-transport-layer side in the PPS21 device, inducing an optical effect in the device accompanied by an increase of the vibrational peak in the PPS21 device.

In conclusion, a high-quantum-efficiency deep-blue PHOLED with CIE coordinates of (0.14,0.16) was developed using novel high-triplet-energy bipolar host materials with a carbazole and two phosphine oxide or sulfide units. The phosphine oxide was more effective than the phosphine sulfide for the electron injection, and a quantum efficiency of 19.2% corresponding to the maximum theoretical quantum efficiency of the PHOLEDs was achieved in the deep-blue PHOLEDs with the PPO21 high-triplet-energy host material for the first time. The development of the bipolar host material, PPO21, was critical to the high quantum efficiency due to charge balance in the light-emitting layer. 100% internal quantum efficiency was obtained and it is expected that further development of bipolar host materials may enable the development of a deep-blue PHOLEDs with an external quantum efficiency over 20%.

Experimental

Synthesis of 3-Bromo-9-(4-bromophenyl)-9-carbazole (2): To a solution of 1 (1.00 g, 3.1 mmol; see Scheme 1)^[18] in N,N-dimethylformamide, a solution of N-bromosuccinimide (0.73 g, 3.1 mmol) was added dropwisely at 0 °C. The mixture was then stirred overnight at room temperature. The solution was diluted with water (20 mL) and extracted with dichloromethane. After solvent removal, the crude product was purified by recrystallization with an ethyl alcohol and gave white solids.

Synthesis of 3-(diphenylphosphino)-9-(4-(diphenylphosphino)phenyl)-9-carbazole (3): Into a 100 mL two-neck flask was placed 2 (2.00 g, 4.98 mmol) in THF (30 mL). The reaction flask was cooled to -78 °C and *n*-butyl lithium (10 m in hexane, 1.14 mL) was slowly added dropwise. The whole solution was stirred at this temperature for 3 h, followed by the addition of chlorodiphenylphophine (2.53 g, 11.4 mmol) under argon atmosphere. The resulting mixture was gradually warmed to ambient temperature, quenched with methanol (10 mL), and extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The white powdery product was obtained to 1.45 g (32%).

Synthesis of 3-(diphenylphosphoryl)-9-(4-(diphenylphosphoryl)phenyl)-9-carbazole (PPO21): A mixture of 3 (1.45 g, 2.37 mmol), dichloromethane (50 mL), and hydrogen peroxide (10 mL) was stirred overnight at room temperature. The organic layer was separated and washed with dichloromethane and distilled water. The extract was dried in vacuum, affording a white solid of PPO21 in 97% yield. $T_g = 111^{\circ}$ C. ¹H NMR (200 MHz, CDCl₃, δ): 8.59–8.53 (d, 1H), 8.11–7.97 (d, 3H), 7.93–7.71 (m, 10H), 7.67 (m, 3H), 7.60–7.45 (m, 13H), 7.36–7.26 (m, 2H). Fast-atom bombardment (FAB) MS *m/z*: 643 [M + 1]⁺.

Synthesis of 3-(diphenylphosphorothioyl)-9-(4-(diphenylphosphorothioyl)-phenyl)-9H-carbazole (PPS21): To a dichloromethane solution of **3** (1g, 1.63 mmol) was added sulfur (0.12g, 3.92 mmol) at room temperature for 6 h. After the addition of water, extraction with dichloromethane and evaporation of the solvent gave a white powder of PPS2197% yield. $T_g = 120 \,^{\circ}$ C. ¹H NMR (200 MHz, CDCl₃, δ): 8.63–8.56 (d, 1H), 8.11–8.07 (d, 3H), 8.01–7.94 (m, 4H), 7.90–7.63 (m, 7H), 7.53–7.45 (m, 13H), 7.36–7.32 (m, 3H). FAB MS *m/z*: 675 [M + 1]⁺.

Measurements: ¹H NMR spectra were obtained on a Varian 200 (200 MHz) spectrometer. PL spectra were recorded on a fluorescence spectrophotometer (HITACHI, F-7000) and UV–vis spectra were obtained







using a UV-vis spectrophotometer (Shimadzu, UV-2501PC). The DSC measurements were carried out on a Mettler DSC 822 instrument under nitrogen at a heating rate of 10 °C min⁻¹. Low- and high-resolution mass spectra were recorded on a JEOL JMS-AX505WA spectrometer in FAB mode. The energy levels of the materials were determined by cyclo voltammetry (CV) and UV-vis absorption, and the device performances of the blue PHOLEDs was measured with a Keithley 2400 source measurement unit and a CS1000 spectroradiometer.

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