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Triaryl Boron Derivatives of Pyridine as Electron Transporting Materials for Blue Phosphorescent Organic Light-emitting Diodes

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ABSTRACT

Two duryl borane derivatives, tris(2,3,5,6-tetramethyl-4-(pyridin-3-*yl*)phenyl)borane (**TDPB**) and tris(2,3,5,6-tetramethyl-4'-(pyridin-3-*yl*)biphenyl-4-*yl*)borane (**TDPPB**), which contain heteroaromatic pyridine rings at peripheral positions were synthesized to investigate the effects of bridging phenyl group on their thermal, photophysical, and electrochemical properties. Upon adding a phenyl unit between duryl and pyridine units, **TDPPB** showed slightly higher thermal stability ($T_d = 446$ °C and $T_g = 166$ °C) than **TDPB** ($T_d = 439$ °C and $T_g = 142$ °C). Both **TDPB** and **TDPPB** have deep highest occupied molecular orbital levels to block the holes/excitons and appropriate lowest unoccupied molecular orbital levels for smooth electron injection. Notably, **TDPB** and **TDPPB** exhibited relatively high triplet energies of 2.84 eV and 2.69 eV, respectively. Thus, the triplet energy level of **TDPB** is sufficient for use in bis[2-(4,6-difluorophenyl)pyridinato-C²,N](picolinato)iridium(III) (**FIrpic**) based blue phosphorescent organic light-emitting diodes (PHOLEDs) as an electron transport material. Accordingly, **TDPB** was used as an electron transport material in **FIrpic**based blue PHOLEDs and the optimized device showed high external quantum efficiency of up to 18.8 %.

1. Introduction

Triaryl boron based compounds have been widely investigated owing to their unique structural and electronic properties such as a triangular planar structure, existence of a vacant p orbital allowing effective orbital interaction with π -conjugated compounds, relatively high Lewis acidity, and a π electron-accepting property in the excited state. Thus, when manipulating molecules with borane, it is possible to synthesize elaborate π -functional materials with effective photophysical and electronic properties using the properties of boron-based compounds.

In particular, trivalent boron compounds can act as an electron-accepting group in donor– acceptor dyad systems owing to their electron-deficient nature.^{1,2} Thus, by attaching an electron-donating group such as pyridine to a boryl compound, the latter can exhibit intramolecular charge transfer (CT) transitions. Therefore, it is possible to apply a substance having a specific photophysical characteristic to the photochemical field, e.g., non-linear optical materials,^{3,4} two-photon absorption materials,^{5,6} and in particular, electron transport materials (ETMs),^{7–9} or emitting materials¹⁰⁻¹² in organic light-emitting diodes (OLEDs).

The essential materials in OLED devices can be roughly classified into three types: hole transport material, emitting material, and ETM. To achieve high efficiency in OLED devices, it is necessary to develop materials with suitable properties for each layer. For example, materials for charge transport layers, *i.e.*, hole transport layer (HTL) and electron transport layer (ETL), must have suitable energy levels and high charge mobility to effectively transfer holes and electrons, respectively, to generate excitons with high quantum yield.¹³ In this

regard, various strategies have been attempted to develop highly efficient HTL^{14} and ETL^{15-17} materials. Accordingly, triarylborane-based materials are utilized as HTL^{18} and ETL^{7-9} in OLEDs. In particular, Kido *et al.* report tris[3-(3-pyridyl)mesityl]borane as an electron transporting material which has a wide HOMO–LUMO energy gap (3.45 eV) and a high triplet excited energy level (2.95 eV).^{7,19}

In this work, a series of duryl borane derivatives, tris(2,3,5,6-tetramethyl-4-(pyridin-3yl)phenyl)borane (**TDPB**) and tris(2,3,5,6-tetramethyl-4'-(pyridin-3-yl)biphenyl-4-yl)borane (**TDPPB**), is designed and synthesized to study structure-property relationship. The chemical structures of **TDPB** and **TDPPB** are illustrated in Chart 1. In this molecular design, we expect that they can be used as ETMs in OLEDs because, owing to the presence of a vacant *p* orbital at the boron center, effective orbital interactions with π -conjugated pyridine-based peripheral groups are possible. In this regard, the effects of phenyl bridge on the thermal, photophysical, and electrochemical properties of **TDPB** and **TDPPB** were systematically investigated. Furthermore, the nature of their excited states was investigated using density functional theory (DFT) calculations and the results were compared with the experimental results. Finally, a bis[2-(4,6-difluorophenyl)pyridinato- C^2 , N](picolinato)iridium(III) (**FIrpic**) based blue phosphorescent device was fabricated with **TDPB** as an ETM and the optimized device showed a relatively high external quantum efficiency (EQE) of up to 18.8 %.



TDPPB

Chart 1. Chemical structures of TDPB and TDPPB.

2. Experimental

2.1. General information

All the experimental procedures were performed under a dry nitrogen or argon atmosphere using standard Schlenk techniques. All solvents were distilled freshly and used under dry nitrogen or argon purging. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Fourier 300 MHz spectrometer operated at 300.1 and 75.4 MHz, respectively. ¹H and ¹³C NMR chemical shifts were measured in CDCl₃ and CD₂Cl₂. Referenced to the relative peaks of CDCl₃ and CD₂Cl₂ are 7.26 and 5.32 ppm for ¹H NMR and 77.16 and 54.00 ppm for ¹³C NMR, respectively. Elemental analyses were performed using a Carlo Erba Instruments CHNS-O EA 1108 analyzer. A high-resolution mass spectrometry (HR-MS) analysis was performed using a highly sensitive liquid chromatography-multistage MS (LC/MS/MSⁿ) (n = 10) spectrometer (Thermo Fisher Scientific, LCQ Fleet Hyperbolic Ion Trap MS/MS^{*n*} Spectrometer). Cyclic voltammetry (CV) was performed in an electrolytic solution prepared using 0.1 M tetrabutyl ammonium hexafluorophosphate (NBu₄PF₆) at room temperature under an atmosphere of argon. For this purpose, CHI600E was used. Glassy carbon, platinum wire, and Ag/AgNO₃ (0.1 M) were used as the working, counter, and reference electrodes, respectively. All the potentials were calibrated to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. 1,4-Dibromobenzene, boron trifluoride diethyl etherate, trimethyl borate, 1,2,4,5-tetramethylbenzene, 3-bromopyridine, potassium bis(pinacolato)diboron, carbonate. potassium acetate, tetrakis(triphenylphosphine)palladium(0), and n-BuLi (2.5 M solution in n-hexane) were purchased from Aldrich or TCI and used without further purification. The starting materials, **(1).**²⁰ **(2)**,²¹ 1,4-dibromo-2,3,5,6-tetramethylbenzene *tris*(bromoduryl)borane 3pyridinylboronic acid (3),²² and 3-(4-bromophenyl)pyridine²³ were prepared according to previously reported procedures.

2.2. Synthesis

3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine (4) A mixture of 3-(4bromophenyl)pyridine (1.4 g, 6 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2dioxaborolane) (2.28 g, 9 mmol), Pd(PPh₃)₂Cl₂ (0.25 g, 0.3 mmol), and KOAc (1.76 g, 18 mmol) in 1,4-dioxane (35 mL) was stirred at 100 °C for 5 h under argon atmosphere. After cooling to room temperature, the mixture was poured into distilled water and extracted with dichloromethane. The combined organic layers were dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified via silica-gel column chromatography using ethyl acetate/*n*-hexane = 1/1(v:v) as an eluent. The resulting oily product was dissolved in dichloromethane and evaporated. Yield: 77%; ¹H NMR (300 MHz, CDCl₃, δ): 8.84–8.83 (d, *J* = 3 Hz, 1H), 8.57–8.55 (m, 1H), 7.91–7.88 (m, 2H), 7.87–7.84 (m, 1H), 7.58–7.55 (m, 2H), 7.35–7.30 (m, 1H), 1.33 (s, 12H), ¹³C NMR (75 MHz, CDCl₃, δ): 150.5, 149.4, 147.8, 139.3, 138.8, 137.2, 136.1, 136.0, 135.9, 131.8, 131.7, 131.7, 131.6, 123.3, 31.0, 20.4.

tris(2,3,5,6-Tetramethyl-4-(pyridin-3-yl)phenyl)borane (TDPB) A mixture of tris(4bromo-2,3,5,6-tetramethylphenyl)borane (3) (1.06 g, 1.63 mmol), 3-pyridinylboronic acid (1) (0.8 g, 6.52 mmol), *tetrakis*(triphenylphosphine)palladium (0.04 g, 0.03 mmol), and 2 M K_2CO_3 (4.9 mL, 9.78 mmol) in toluene/ethanol (v:v = 12 mL/4 mL) was stirred at 80 °C for 48 h under argon atmosphere. After cooling to room temperature, the mixture was poured into distilled water and extracted with dichloromethane. The combined organic layers were dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified via silica-gel column chromatography using ethyl acetate as an eluent. The resulting white solid was dissolved in dichloromethane and evaporated. Yield: 81%; ¹H NMR (300 MHz, CDCl₃, δ): 8.60–8.59 (d, J = 3.6 Hz, 3H), 8.41 (s, 3H), 7.50–7.48 (d, 3H), 7.39–7.34 (m, 3H), 2.07 (b, s, 18H), 1.85 (b, s, 18H), ¹³C NMR (75 MHz, CDCl₃, δ): 150.5, 149.4, 147.8, 139.3, 138.8, 137.2, 136.1, 136.0, 135.9, 131.8, 131.7, 131.7, 131.6, 123.3, 31.0, 20.4. HRMS (FAB) calcd for C₄₅H₄₈BN₃: 641.3941, found 641.3939; Elem. anal. calcd for C₄₅H₄₈BN₃: C, 84.23; H, 7.54; B, 1.68; N, 6.55; Si, 4.72. Found: C, 84.22; H, 7.52; N, 6.56.

tris(2,3,5,6-Tetramethyl-4'-(pyridin-3-yl)biphenyl-4-yl)borane (TDPPB) A mixture of tris(4-bromo-2,3,5,6-tetramethylphenyl)borane (3) (0.74 g, 1.15 mmol), 3-(4-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine (1.3)4.6 (5) g, mmol). tetrakis(triphenylphosphine)palladium (0.07 g, 0.06 mmol), and K₂CO₃ (0.95 g, 6.9 mmol) in THF/H₂O (v:v = 12 mL/4 mL) was stirred at 80 °C for 48 h under argon atmosphere. After cooling to room temperature, the mixture was poured into distilled water and extracted with dichloromethane. The combined organic layers were dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified via silica-gel column chromatography using ethyl acetate as an eluent. The resulting white solid was dissolved in dichloromethane and evaporated. Yield: 80%; ¹H NMR (300 MHz, CD₂Cl₂, δ): 8.93–8.92 (m, 3H), 8.58–8.56 (m, 3H), 8.00–7.96 (m, 3H), 7.71–7.67 (m, 6H), 7.42–7.38 (m, 3H), 7.28–7.25 (m, 6H), 2.12 (b, s, 18H), 1.91 (b, s, 18H), 13 C NMR (75 MHz, CD₂Cl₂, δ): 148.7, 148.0, 147.8, 142.8, 142.2, 135.9, 135.4, 135.3, 133.7, 131.0, 129.9, 126.5, 123.1, 19.6, 19.3. HRMS (FAB) calcd for C₆₃H₆₀BN₃: 869.4880, found 869.4882; Elem. anal. calcd for C₆₃H₆₀BN₃: C, 86.98; H, 6.95; B, 1.24; N, 4.83. Found: C, 86.99; H, 6.94; N, 4.84.

2.3. Absorption and emission spectra

The absorption and photoluminescence spectra were recorded using a SHIMADZU UV-2450 UV-vis–NIR scanning spectrophotometer and a VARIAN Cary Eclipse fluorescence spectrophotometer, respectively.

2.4. Phosphorescence emission spectra

At 77 K, the third harmonic (355 nm) pulse of a Q-switched Nd:YAG laser (neodymiumdoped yttrium aluminum garnet; Continuum, Surelite II; pulse width of 4.5 ns) was used to excite the molecules. The phosphorescence spectra were recorded using an ICCD detector (Andor, iStar) equipped with a monochromator (DongWoo Optron, Monora 500i). The temporal profiles were measured using a monochromator equipped with a photomultiplier (Zolix Instruments Co., CR 131) and a digital oscilloscope (Tektronix, TDS-784D). Oxygen in the sample solutions was removed via the argon purging method.

2.5. Thermal properties

Thermogravimetric analysis (TGA) was performed using a TGA/DSC 1 (Mettler-Toledo Inc.) instrument. TGA was conducted several times, and the data were confirmed. The sample was loaded into a weight-tared alumina pan, and heated at a rate of 5 °C/min from 25 to 800 °C under nitrogen flow (50 mL/min). The thermal properties were measured using differential scanning calorimetry (DSC; Pyris Diamond DSC; Perkin Elmer). The compound was first melted at a heating rate of 10 °C/min and subsequently cooled at a rapid rate of 40 °C/min until room temperature.

2.6. DFT calculations

The derivatives were theoretically calculated using the *Gaussian 09 package*.²⁴ The groundstate geometries of the compounds were optimized using the B3LYP DFT and the 6/31G(d,p) basis set. The contours of electron density were plotted using *Chem3D ver.10.*²⁵

2.7. Device fabrication and characterization

The OLED devices were fabricated on glass substrates pre-coated with a 150-nm-thick indium tin oxide (ITO) layer having a sheet resistance of 10 Ω square⁻¹. The ITO glass was pre-cleaned using a conventional solvent cleaning method. The ITO surface was cleaned again with UV ozone treatment immediately before depositing the hole injection layer. The organic, Liq, and Al layers were deposited sequentially onto the substrate without breaking the vacuum. The current–voltage characteristics of the OLEDs were measured using a source measure unit (Keithley 2635B). The electroluminescence spectra, luminance, and CIE coordinates were measured using a spectroradiometer (Konica Minolta CS-2000). Assuming Lambertian emission, the EQE was calculated using the luminance, current density, and electroluminescence spectrum.

3. Results and Discussion



Scheme 1. Synthesis of TDPB and TDPPB.

3.1. Synthesis

Scheme 1 illustrates the synthetic procedures used for the preparation of **TDPB** and **TDPPB**. Initially, the starting compounds were prepared according to the previously reported procedures. Briefly, 1,4-dibromo-2,3,5,6-tetramethylbenzene (1) was obtained via

bromination reaction at 1 and 4 positions of 2,3,5,6-tetramethylbenzene with bromine solution in dichloromethane with a yield of 64%. tris(Bromoduryl)borane (**2**) was synthesized via mono-lithiation of (**1**) followed by the addition of boron trifluoride diethyl etherate. 3-Pyridinylboronic acid (**3**) was synthesized by conducting a direct substitution reaction between 3-bromopyridine and trimethyl borate to obtain a monosubstituted product. **TDPB** was prepared via palladium-catalyzed Suzuki–Miyaura coupling reaction in the presence of excess amounts of base as a white solid with a yield of 81%. Similarly, **TDPPB** was prepared via Suzuki–Miyaura coupling reaction of (**2**) with 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-*yl*)phenyl)pyridine (**4**) in the presence of Pd(PPh₃)₄ as a catalyst and excess amounts of base as a white solid with a yield of 80%. The structures and chemical purities of the final products were adequately verified using ¹H NMR and ¹³C NMR, mass spectrometry, and elemental analysis (see Experimental Section).

3.2. Thermal properties

The thermal properties of **TDPB** and **TDPPB** were investigated using TGA and DSC under a nitrogen environment at a heating rate of 10 °C min⁻¹. Upon adding a phenyl unit between duryl and pyridine units, **TDPPB** showed higher thermal stability with the thermal decomposition temperature (T_d) of 446 °C as compared with that of **TDPB** at 439 °C, as shown in Electronic Supplementary Information, Figure S1. In addition, high thermal stability with a high glass transition temperature is desirable in OLED device fabrication process because it can prevent morphological changes and suppress the formation of aggregation upon heating. In this regard, the glass transition temperatures of **TDPB** and **TDPPB** were investigated using DSC. The results are illustrated in Figure 1 and summarize d in Table 1. The glass transition temperatures (T_e) of **TDPB** and **TDPPB** were measured to

be 142 and 166 °C, respectively. The improvement in T_d and T_g of **TDPPB** compared with the corresponding values of **TDPB** might be attributed to the higher molecular weight.



Figure 1. Glass transition temperatures (T_g) of **TDPB** and **TDPPB** analyzed using DSC scan rate at 10 °C min⁻¹.

Table 1. Thermal, photophysical, and electrochemical properties of TDPB and TDPPB

	T _d (°C)	T _g (°C)	$\lambda_{abs}^{a}(nm)$	$\frac{\lambda_{\rm em}}{{\rm RT}^a}$	(nm) 77 K ^b	$E_{\rm T}({\rm ev})$	$E_{\rm red}^{a}({\rm V})$	HOMO ^c (eV)	LUMO ^d (eV)	$E_{\rm g}({\rm eV})$
TDPB	439	142	243, 330	403	436	2.84	-1.12	-6.47	-2.98	3.49
TDPPR	446	166	256, 279, 331	404	461	2.69		-6.41	-2.95	3.46

^{*a*}Measured in dichloromethane at room temperature, ^{*b*}measured in 2-MeTHF at 77 K, ^{*c*} E_{HOMO} (eV) = $E_{\text{LUMO}} - E_{\text{g}}$, and ^{*d*} E_{LUMO} (eV) = $-e(E_{\text{red}}(\text{V vs. Fc/Fc}^+) + 4.8 \text{ eV})$.

3.3. Photophysical properties

Steady-state absorption and emission spectra of **TDPB** and **TDPPB** were measured in dichloromethane solution at room temperature and the resulting spectral data are summarized in Table 1. As shown in Figure 2, the two compounds exhibited similar absorption spectra but different intensities depending on the phenyl bridge units. **TDPPB** showed a hyperchromic shift compared with **TDPB** without significant changes in wavelength. The absorption peaks at approximately 250 nm are mainly attributed to the ligand-centered π - π * transitions,

whereas the absorption peaks at approximately 330 nm are assigned to the CT band from the duryl units to the central boron atom in the molecule¹⁸ which supported by DFT calculations (*vide infra*).



Figure 2. UV–vis absorption and photoluminescence spectra of **TDPB** and **TDPPB** in 5 μ M dichloromethane solution. Photoluminescence spectra were obtained via excitation at 330 nm.

The photoluminescence spectra of **TDPB** and **TDPPB** in dichloromethane solution were also similar to each other, as shown in Figure 2. Notably, **TDPPB** shows an identical emission spectrum to that of **TDPPB** even though it has a lengthened conjugation in the molecular structure. We obtained the solvent-dependent emission spectra to determine the origin of emission. As **TDPB** and **TDPPB** are donor–acceptor type dyad compounds, the CT state in the excited states would be formed. Therefore, the sensitivity of the solvent to polarity can be analyzed in terms of the difference between the dipole moments in the ground and excited states. As shown in Figure S2, no significant solvatochromic shifts were observed in both compounds in the absorption spectra, whereas the emission spectra were red-shifted with the increase in solvent polarity, which indicates the presence of CT state in the excited state. Thus, the emissions of **TDPB** and **TDPPB** originated from the CT state and had a similar wavelength even though the two compounds have different conjugation lengths. The

CT phenomenon was analyzed using a Lippert–Mataga plot (Figure 3), a plot of the Stokes shift of the emission versus the solvent polarity.²⁶ The difference (Stokes shift) between the maximum absorption and emission wavelengths, in wavenumbers (Δv), is expressed using equation (1):

$$\overline{\nu}_{a} - \overline{\nu}_{f} = \left(\frac{2}{hca_{0}^{3}}\right) \times \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n - 1}{2n + 1}\right) \times \left(\mu_{e} - \mu_{g}\right)^{2} = \left(\frac{2}{hca_{0}^{3}}\right) \times (\Delta\mu)^{2} \times \Delta f \quad (1)$$

where $\mu_e - \mu_g (\Delta \mu)$ is the difference between the dipole moments of the excited and ground states, c is the speed of light, h is Planck's constant, and a_0 is the radius of the Onsager cavity around the fluorophore. The dielectric constant (ε) and the refractive index (n) of the solvents are included in the term Δf , known as orientation polarizability. The Onsager radius was considered as half the average of 6.7 and 10.9 Å for compounds TDPB and TDPPB, respectively, which were calculated from the optimized structures obtained using DFT calculations (B3LYP method, 6-31G(d,p) basis using Gaussian program²⁴). As shown in Figure 3, the Stokes shift for the CT emissions in various solvents changed linearly with Δf . Using equation (1), the dipole moment differences between the excited state and ground state $(\Delta \mu)$ for **TDPB** and **TDPPB** were estimated to be 4.53 and 7.68 Debye, respectively, as listed in Table 1. As expected, $\Delta \mu$ of **TDPPB** was larger than that of **TDPB** because **TDPPB** has a longer distance between the electron donor and electron acceptor groups. This solventdependent emission is consistent with the presence of a highly polarized excited state, thus confirming that the lowest unoccupied molecular orbital (LUMO) level is dominated by the empty p orbital of the boron atom and the lowest energy electronic transition is a CT from the peripheral aryl groups to the boron center.



Figure 3. Lippert–Mataga plots for **TDPB** and **TDPPB** (1: in *n*-hexane, 2: THF, 3: dichloromethane, and 4: acetonitrile).

The triplet energy levels of host, HTL, and ETL materials are important factors for the application in phosphorescent OLEDs (PHOLEDS) because the back energy transfer from the triplet of the dopant to the triplet of the host or adjacent layers will reduce the emission efficiency. In this regard, the triplet energy levels of **TDPB** and **TDPPB** were measured in 2-methyltetrahydrofuran (2-MeTHF) at 77 K. As shown in Figure 4, **TDPB** showed a higher triplet energy level (437 nm, 2.84 eV) than **TDPPB** (461 nm, 2.69 eV), which were estimated by considering the highest peak energy of phosphorescence as the transition energy of $T_1 \rightarrow S_0$, which corresponded to the vibronic 0-0 transition between these two electronic states. The higher triplet energy level of **TDPB** compared with that of **TDPPB** might be due to its shorter conjugation length. Notably, the triplet energy level of **TDPB** is sufficiently higher than that of **FIrpic** ($T_1 = 2.6 \text{ eV}$),²⁷ a phosphorescent dopant that emits blue light. Therefore, we expect that the utilization of **TDPB** as an electron transporting layer in **FIrpic** based blue devices would effectively confine the triplet excitons on the dopant and prevent the back energy transfer process.



Figure 4. Phosphorescence spectra of **TDPB** (top) and **TDPPB** (bottom) measured in 2-MeTHF at 77 K.

3.4. Electrochemical properties

To investigate the electrochemical properties of **TDPB** and **TDPPB**, CV was performed by employing a three-electrode cell system; a glassy carbon electrode was used as the working electrode, whereas a platinum wire and Ag/AgNO₃ were used as the counter and reference electrodes, respectively. As shown in Figure 5, **TDPB** and **TDPPB** showed reduction waves at -1.30 (E_{pc}) and -1.12 V (E_{pa}), and -1.33 (E_{pc}) and -1.11 V (E_{pa}) (versus Fc/Fc⁺), respectively. These peaks can be ascribed to the duryl borane unit in its reduced form. Using redox potentials and the optical band gap calculated from the edge of the absorption spectra, the energy levels of the highest occupied molecular orbital (HOMO) in **TDPB** and **TDPPB** were estimated to be -6.47 and -6.41 eV, respectively, and those of the LUMO in **TDPB** and **TDPPB** were estimated to be -2.98 and -2.95 eV, respectively. Notably, the relatively low LUMO energy levels of **TDPB** and **TDPPB** might form a low electron-injection barrier and thus result in a low driving voltage when they are applied to OLED devices. Furthermore, the deep HOMO levels of **TDPB** and **TDPPB** can be an additional advantage when they are applied to OLED devices because they can act as hole blocking materials and prevent exciton quenching process occurring owing to hole leakage into the ETL.²⁸



Figure 5. CV curves of TDPB and TDPPB in dichloromethane solution containing 0.1 M NBu₄PF₆ as electrolyte, at a scan rate of 0.1 V s⁻¹.

3.5. DFT calculations

To gain insight into the electronic properties of the compounds, the DFT calculations of the frontier molecular orbitals were performed by using the B3LYP/6-31G(d,p) method with the *Gaussian 09 package*.²⁴ In the optimized structure of **TDPB**, the inner duryl groups and peripheral pyridine groups are significantly twisted together with averaged dihedral angles of 99.7° owing to the steric hindrance of tetramethyl groups. Similarly, the inner duryl groups and bridged phenyl groups in **TDPPB** are also in perpendicular positions with averaged dihedral angles of 99.7°. In contrast, the bridged phenyl groups and peripheral pyridine groups in **TDPPB** are in horizontal positions with averaged dihedral angles of 161.6°. Figure 6 shows the orbital distributions for the HOMO and LUMO of **TDPB** and **TDPPB** and **TDPPB** are mainly located on the duryl groups, and the LUMOs were mainly located on

the electron-deficient central boron atom. Time-dependent DFT (TD-DFT) with the same functional and basis set confirms the origin of the main transitions of **TDPB** and **TDPPB** at approximately 330 and 250 nm, as shown in Figure S4 and Table S1. The lowest energy absorption λ_{max} at approximately 330 nm is mainly associated with the CT transitions from the duryl units to the central boron atom in the molecule, whereas the absorption λ_{max} at approximately 250 nm is mainly attributed to the ligand-centered π - π * transitions in duryl– pyridine groups. The additional strong transition for **TDPPB** at approximately 275 nm is attributed to the π - π * transitions in phenyl-pyridine groups, as shown in Figure S4. According to the results of TD-DFT calculation, we ascertained that the hyperchromic shift in **TDPPB** is due to the presence of additional bridged phenyl groups. These results are consistent with the experimental results.



Figure 6. Optimized structures of **TDPB** and **TDPPB** with their HOMO and LUMO orbital distributions calculated using DFT calculations.

3.6. Electron Only Device (EOD)

EODs for **TDPB** and **TPBi** (2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole)) were fabricated to verify the electron transport property of **TDPB**. **TPBi** was chosen because

it is well-known and widely used ETM. A similar device was not prepared with **TDPPB** because this compound was decomposed during the train-sublimation process. Figure 7 shows the current density–voltage (J–V) characteristics of EOD with the structure of ITO (150 nm)/Al (100 nm)/**TDPB** or **TPBi** (50 nm)/Liq (1 nm)/Al (150 nm). According to the space-charge-limited current (SCLC) model, which is characterized by field-dependent mobility,^{29,30} the electron mobility (μ) of **TDPB** was estimated to be 1.24 × 10⁻³ cm² V⁻¹ s⁻¹ at 1 MV cm⁻¹, which is significantly higher than that of **TPBi** (2.46 × 10⁻⁵ cm² V⁻¹ s⁻¹ at 1 MV cm⁻¹). The high electron mobility of **TDPB** at low driving voltage may result from such a coordination effect of the nitrogen atom in peripheral heteroaromatic rings of **TDPB** with lithium cations, which induces an effective electron injection.³¹



Figure 7. (a) J–V characteristics of EOD with **TDPB** and **TPBi**. The devices were fabricated with the following structure: ITO (150 nm)/Al (100 nm)/ **TDPB** or **TPBi** (50 nm)/Liq (1 nm)/Al (150 nm) and (b) the J–V characteristics were fitted to SCLC with field-dependent mobility. $J = (9/8)_{\varepsilon_0 \varepsilon_r} (E^2/L)_{\mu_0} \exp(0.89)\beta\sqrt{E}$, where J is the current density; $\varepsilon_0 \varepsilon_r$ is the dielectric constant; *E* is the electric field; *L* is the film thickness; μ_0 is the zero-field carrier mobility; β is the Poole–Frenkel factor. The values of μ_0 and β were calculated by assuming that ε_r is equal to 3. The field-dependent mobility was calculated using the Poole–Frenkel equation: $\mu(E) = \mu_0 \exp(\beta\sqrt{E})$.

3.7. Device Performance

To examine **TDPB** as an ETM, PHOLEDs were fabricated with the structure of ITO (150 nm)/HATCN (10 nm)/TAPC (x nm)/mCBP:FIrpic 8% (30 nm)/TDPB(y nm)/Liq (1 nm)/Al (150)nm), where HATCN dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11is hexacarbonitrile, **TAPC** is 4,4'-cyclohexylidene-bis[*N*,*N*-bis(4-methylphenyl)benzenamine], and **mCBP** is 3,3-di(9*H*-carbazol-9-*yl*)-biphenyl. The chemical structures and the energy level diagram of the used materials are shown in Figure S5. To optimize the efficiency, five different devices were fabricated with variations of the thickness of HTL and ETL; device 1: HTL 85 nm, ETL 30 nm, device 2: HTL 100 nm, ETL 30 nm, device 3: HTL 70 nm, ETL 30 nm, device 4: HTL 70 nm, ETL 35 nm, and device 5: HTL 85 nm, ETL 35 nm. The performances of the five devices are summarized in Figure 8 and Table 2. Among the five devices, device 4 showed the best performance with the peak external electroluminescence quantum and power efficiencies of $\eta_{ext} = 18.8\%$ and $\eta_p = 31.3 \text{ lm W}^{-1}$, respectively.



Figure 8. (a) Current density–voltage–luminance curves, (b) quantum efficiency–luminance curves, and (c) electroluminescence spectra of devices 1–5.

	Current Efficiency (cd/A)			Power Efficiency (lm/W)			EQE (%)			Turn-On Voltage (V)	CIE (x, y)
	Max	100 nits	1000 nits	Max	100 nits	1000 nits	Max	100 nits	1000 nits	(at 1 nits)	(at 400 nits)
Device 1	34.83	32.77	17.40	30.38	22.39	7.79	17.44	16.51	8.74	3.44	0.14, 0.33
Device 2	36.11	33.42	13.00	30.34	21.94	5.20	17.12	15.96	6.14	3.53	0.15.0.36
Device 3	33.44	31.25	19.30	31.17	21.13	9.30	17.91	16.26	10.06	3.39	0.15, 0.31
Device 4	36.76	33.36	12.33	31.13	20.72	4.86	18.84	17.23	6.34	3.53	0.15, 0.32
Device 5	34.76	33.64	16.00	27.46	22.96	7.15	17.42	16.96	8.04	3.58	0.15, 0.33

Table 2. Summary of the PHOLED devices 1-5

Device 1: ITO(150 nm)/HATCN(10 nm)/TAPC(85 nm)/mCBP:FIrpic 8%(30 nm)/**TDPB**(30 nm)/Liq(1 nm)/Al(150 nm). **Device 2**: ITO(150 nm)/HATCN(10 nm)/TAPC(100 nm)/mCBP:FIrpic 8%(30 nm)/**TDPB**(30 nm)/Liq(1 nm)/Al(150 nm). **Device 3**: ITO(150 nm)/HATCN(10 nm)/TAPC (70 nm)/mCBP:FIrpic 8%(30 nm)/**TDPB**(30 nm)/Liq(1 nm)/Al(150 nm). **Device 4**: ITO(150 nm)/HATCN(10 nm)/TAPC (70 nm)/mCBP:FIrpic 8%(30 nm)/**TDPB**(35 nm)/Liq(1 nm)/Al(150 nm). Device 5: ITO(150 nm)/HATCN(10 nm)/TAPC(85 nm)/mCBP:FIrpic 8%(30 nm)/TDPB(35 nm)/Liq(1 nm)/Al(150 nm).

4. Conclusions

In this study, two duryl borane derivatives, **TDPB** and **TDPPB**, which contain heteroaromatic pyridine rings at peripheral positions, were prepared and their thermal, photophysical, and electrochemical properties were systematically investigated. **TDPB** and **TDPPB** showed high thermal stabilities with T_g values at 142 and 166 °C, respectively. Low LUMO energy levels ($\approx 2.96 \text{ eV}$) and deep HOMO energy levels ($\approx 6.45 \text{ eV}$) of both compounds would be beneficial when they are applied in OLED devices because they would form a low electron-injection barrier and may act as a hole-blocking material. The triplet energies of these compounds can be tuned from 2.69 to 2.84 eV by shortening the conjugation length, and **TDPB** shows the higher value of 2.84 eV. The electron mobility (μ) of **TDPB** was estimated to be $1.24 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an optimized FIrpic-based blue phosphorescence device with **TDPB** achieved a maximum EQE of 18.84% with the CIE coordinates of (0.15, 0.32). These results suggest that these duryl borane derivatives can be used as high-efficient blue phosphorescent ETMs.

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6. References

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Highlights

- ✓ Two boron derivatives of pyridine were synthesized and systematically investigated their thermal, photophysical, and electrochemical properties.
- ✓ Among the series, **TDPB** compound has proper properties as ETM; high thermal stability with Tg value of 142 °C, high triplet energy of 2.84 eV, proper LUMO energy level of −2.98 eV, and deep HOMO energy level of −6.47 eV.
- ✓ EOD using **TDPB** showed relatively high electron mobility with 1.24×10^{-3} cm² V⁻¹ s⁻¹ at 1 MV cm⁻¹ and optimized FIrpic based blue PhOLEDs device achieved a maximum EQE of 18.84% with the CIE coordinates of (0.15, 0.32).