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## Efficient deep-blue emitters based on triphenylamine-linked benzimidazole derivatives for nondoped fluorescent organic light-emitting diodes

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#### 1. Introduction

Deep-blue fluorescent organic light-emitting diodes (FLOLEDs) possessing high efficiency and pure Commission Internationale de l'Eclairage (CIE) chromaticity coordinates are a prerequisite for full-color displays and lighting devices. There have been many studies on improving the device performance by optimally designing the emitters using doped or nondoped systems [1–3]. Nonetheless, owing to the intrinsic wide bandgap nature of deep-blue emitters, only a few examples of high-performance deep-blue FLOLEDs have been reported, in contrast to red and green fluorescent devices [4–7].

Doping of emitters into host materials in the emitting layer (EML) was mainly involved for the development of high-efficiency deep-blue FLOLEDs. Chen et al. reported an external quantum efficiency (EQE) of 2.3% with CIE coordinates of (0.15,0.11) based on mono(styryl)aminebased deep-blue dopants in FLOLEDs [8]. FLOLED devices fabricated using a 9-anthracene-spirobenzofluorene deriv-

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#### ABSTRACT

Two triphenylamine-substituted benzimidazole derivatives were synthesized for use as efficient deep-blue emitters in nondoped fluorescent organic light-emitting diodes (FLOL-EDs). The molecular design of 4',4''-(1H-benzo[d]imidazole-1,2-diyl)*bis*(*N*,*N*-diphenylbiphenyl-4-amine) (T2B) to limit the molecular packing density enabled T2B-based devices to suppress the exciton quenching by a bulky three-dimensional structure. Nondoped FLOLEDs fabricated using T2B as a blue emitter exhibited an external quantum efficiency of 4.67% with color coordinates of (0.15,0.08).

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ative as the host and a diphenylamine-substituted spirobenzofluorene derivative as the dopant showed an EQE of 5.4% with CIE coordinates of (0.13,0.15) [9]. Deep-blue FLOLEDs based on spirocyclic aromatic hydrocarbon derivatives and purine derivatives exhibited CIE coordinates of (0.16,0.08) with 1.1 cd/A and CIE coordinates of (0.15,0.06) with an EQE of 3.1%, respectively [10,11].

A nondoped system has an advantage of a simple device structure that employs only a single emitting material without using a complicated host–dopant codeposition process [12–16]. However, in this type of system, excimers are usually induced by intermolecular interactions between emitters, or excitons are readily quenched, resulting in a red-shift of the CIE coordinates and/or low quantum efficiency because emitters tend to be closely packed in the EML [17]. Relatively little attention has been paid to the synthesis of deep-blue emitters because EQEs > 2% and CIEy < 0.10 in the deep-blue nondoped system are difficult to obtain simultaneously. Therefore, it is still challenging to design deep-blue emitters for reliable device performance.

In this study, we synthesized deep-blue fluorescentemitting materials, *N*,*N*-diphenyl-4'-(1-phenyl-1Hbenzo[d]imidazol-2-yl)biphenyl-4-amine) (T1B) and







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4',4''-(1H-benzo[d]imidazole-1,2-diyl)bis(N,N-diphenylbiphenyl-4-amine) (T2B), for the development of highly efficient, nondoped FLOLEDs with deep-blue CIE coordinates,where the correlation between the device performanceand the molecular packing density was investigated. FLOL-EDs using sterically bulky T2B as an emitter without a dopant showed deep-blue emissions with a CIEy of 0.08 and anEQE of 4.67% at 100 cd/m<sup>2</sup>, which is better than the valuesobtained from T1B owing to more efficient inhibition ofexciton quenching.

#### 2. Materials and methods

#### 2.1. Materials

*N*-phenyl-o-phenylenediamine, 1-fluoro-2-nitrobenzene, 4-bromobenzaldehyde, 4-(diphenylamino)phenylboronic acid, *tetrakis*(triphenylphosphine) palladium, and sodium carbonate were purchased from Aldrich and used without purification.

#### 2.2. Synthetic procedure

#### 2.2.1. Synthesis of 2-(4-bromophenyl)-1-phenyl-1Hbenzo[d]imidazole (B1)

Acetic acid (20 mL) was added to a flask containing Nphenyl-o-phenylenediamine (1.50 g, 8.14 mmol) and 4bromobenzaldehyde (1.66 g, 8.96 mmol). After the mixture was refluxed for 12 h, distilled water was added and the organic layer was extracted with dichloromethane. The organic layer was washed with sodium bicarbonate and brine and dried using anhydrous sodium sulfate. The filtrate was concentrated in vacuo to give a crude mixture, which was then subjected to column chromatography on silica gel using ethyl acetate and hexane (v/v 1:20) as the eluent. Analytically pure 2-(4-bromophenyl)-1-phenyl-1H-benz[d]imidazole was isolated as a white solid (1.39 g, 49%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87 (d, J = 8.4 Hz, 1H), 7.53–7.42 (m, 7 H), 7.35-7.21 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 151.21, 142.90, 137.25, 136.75, 131.55, 130.84, 130.01, 128.90, 128.77, 127.37, 124.04, 123.58, 123.15, 119.90, 110.48. MALDI-TOF MS: calcd for C<sub>19</sub>H<sub>13</sub>BrN<sub>2</sub> 348.03, found 349.20.

#### 2.2.2. Synthesis of N-(4-bromophenyl)-2-nitroaniline

A mixture of 1-fluoro-2-nitrobenzene (5.00 g, 35.436 mmol), 4-bromoaniline (12.19 g, 70.87 mmol), and potassium fluoride (2.57 g, 44.30 mmol) was heated at 170-180 °C for 72 h. The resulting mixture was extracted with dichloromethane, and the organic layer was washed with water and brine and dried using anhydrous sodium sulfate. The filtrate was concentrated in vacuo and was then subjected to column chromatography on silica gel using dichloromethane as the eluent. The resulting red solid was recrystallized from methanol to afford N-(4-bromophenyl)-N'-(2-nitrophenyl)amine as orange needles (3.10 g, 30%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.37 (s, 1H), 8.19 (d, J = 8.6 Hz, 1H), 7.51 (d, J = 8.6 Hz, 2H), 7.37 (t, J = 7.8 Hz, 1H), 7.24–7.14 (m, 3H), 6.80 (t, J = 7.4 Hz, 1H).  $^{13}\text{C}$  NMR (CDCl\_3, 100 MHz)  $\delta$  142.36, 137.93, 135.73, 133.50, 132.80, 126.74, 125.70, 118.40, 118.04, 115.94.

MALDI-TOF MS: calcd for  $C_{12}H_9BrN_2O_2$  291.98, found 290.37.

#### 2.2.3. Synthesis of N-(4-bromophenyl)-1,2-phenylenediamine

Α suspension of N-(4-bromophenyl)-N'-(2-nitrophenyl)amine (2.00 g,6.85 mmol) and stannous chloride dihydrate (7.73 g, 34.25 mmol) in ethanol was refluxed for 24 h. The reaction mixture was concentrated in vacuo and neutralized with aqueous sodium bicarbonate solution. The resulting solution was extracted with ethyl acetate, dried using anhydrous sodium sulfate, and concentrated in vacuo to afford the crude product. The product was isolated by column chromatography on silica gel using ethyl acetate and hexane  $(v/v \ 1:3)$  as the eluent (1.78 g,99%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26 (d, J = 11.4 Hz, 2H), 7.08–7.01 (m, 2H), 6.80–6.73 (m, 2H), 6.58 (d, J = 8.2 Hz, 2H), 5.16 (s, 1H), 3.71 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 144.53, 142.12, 132.04, 127.70, 126.28, 125.26, 119.17, 116.62, 116.22, 110.95. MALDI-TOF MS: calcd for C<sub>12</sub>H<sub>11</sub>BrN<sub>2</sub> 262.01, found 262.32.

#### 2.2.4. Synthesis of 1,2-bis(4-bromophenyl)-1Hbenzo[d]imidazole (B2)

Acetic acid (20 mL) was added to a flask containing *N*-(4-bromophenyl)-1,2-phenylenediamine (1.0 g, 5.43 mmol) and 4-bromobenzaldehyde (1.21 g, 6.51 mmol). After the mixture was refluxed for 12 h, distilled water was added and the organic layer was extracted with dichloromethane. The organic layer was washed with aqueous sodium bicarbonate solution and brine and dried using anhydrous sodium sulfate. The filtrate was concentrated in vacuo to give a crude mixture, which was then subjected to column chromatography on silica gel using ethyl acetate and hexane  $(v/v \ 1:6)$  as the eluent to afford analytically pure 1,2-bis(4bromophenyl)-1H-benzo[d]imidazole (1.11 g,47%).  $^{1}H$ NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (d, I = 7.8 Hz, 1H), 7.63 (d, J = 7.9 Hz, 2H), 7.43 (dd, J = 8, 12 Hz, 4H), 7.34 (t, J = 7 Hz, 1H), 7.32–7.16 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 151.09, 142.95, 136.91, 135.78, 133.29, 131.74, 130.83, 128.87, 128.57, 124.29, 123.82, 123.40, 122.65, 120.08, 110.22. MALDI-TOF MS: calcd for  $C_{19}H_{12}Br_2N_2$  425.94, found 427.23.

#### 2.2.5. N,N-diphenyl-4'-(1-phenyl-1H-benzo[d]imidazol-2yl)biphenyl-4-amine (T1B)

A mixture of compound B1 (0.70 g, 2.00 mmol), 4-(diphenylamino)phenylboronic acid (0.70 g, 2.40 mmol), tetrakis(triphenylphosphine)palladium (0.12 g, 0.10 mmol), and aqueous sodium carbonate (2 M, 10 mL) in tetrahydrofuran (40 mL) and methanol (10 mL) was heated to reflux in a nitrogen atmosphere for 24 h. After the reaction mixture was concentrated in vacuo, the resulting mixture was extracted with dichloromethane. The organic layer was washed with water and brine and dried using anhydrous sodium sulfate. The filtrate was concentrated in vacuo to give a crude mixture, which was then subjected to column chromatography on silica gel using dichloromethane and hexane (v/v 1:1) as the eluent to afford analytically pure N,N-diphenyl-4'-(1-phenyl-1H-benzo[d]imidazol-2yl)biphenyl-4-amine as a yellow solid (0.78 g, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, I = 8 Hz, 1H), 7.61

(d, J = 8.4 Hz, 2H), 7.52 (d, J = 8 Hz, 4H), 7.45 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.27–7.23 (m, 8H), 7.10 (dd, J = 8.8, 2 Hz, 6H), 7.02 (t, J = 7.2 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  152.18, 147.65, 147.51, 141.39, 137.29, 137.09, 133.66, 129.89, 129.79, 129.28, 128.57, 127.62, 127.47, 127.24, 124.53, 123.62, 123.28, 123.09, 122.98, 119.75, 110.38. MALDI-TOF MS: calcd for C<sub>37</sub>H<sub>27</sub>N<sub>3</sub> 513.22 g/mol, found 513.26 g/mol. HRMS (FAB<sup>+</sup>) [M + H: C<sub>37</sub>H<sub>28</sub>N<sub>3</sub>]: calcd for 514.2283, found 514.2283. Anal. Calcd. For C<sub>37</sub>H<sub>27</sub>N<sub>3</sub>: C, 86.52; H, 5.30; N, 8.18. Found: C, 86.05; H, 5.18; N, 8.11.

#### 2.2.6. Synthesis of 4',4"-(1H-benzo[d]imidazole-1,2diyl)bis(N,N-diphenylbiphenyl-4-amine) (T2B)

Using an approach similar to that used for the synthesis of T1B by the Suzuki coupling reaction, a white powder was obtained (0.65 g, 74%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ) δ 7.89 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.52 (dd, J = 8.4, 2 Hz, 4H), 7.46 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.34–7.23 (m, 11H),  $7.17-7.09 (m, 12H), 7.03 (q, I = 8.4 Hz, 4H), {}^{13}C NMR (CDCl_3, 12H) = 100 COC M + 1$ 100 MHz) δ 152.19, 147.85, 147.65, 147.51, 147.48, 143.09, 141.40, 140.81, 137.32, 135.59, 133.67, 133.17, 129.83, 129.34, 129.28, 128.20, 127.78, 127.72, 127.63, 126.28, 124.61, 124.52, 123.62, 123.28, 123.21, 123.08, 122.99, 119.78, 110.46. MALDI-TOF MS: calcd for C<sub>55</sub>H<sub>40</sub>N<sub>4</sub> 756.33 g/mol, found 756.77 g/mol. HRMS (FAB<sup>+</sup>)[M + H: C<sub>55</sub>H<sub>41</sub>N<sub>4</sub>]: calcd for 757.3331, found 757.3331. Anal. Calcd. For C<sub>55</sub>H<sub>40</sub>N<sub>4</sub>: C, 87.27; H, 5.33; N, 7.40. Found: C, 86.72; H, 5.28; N, 7.30.

#### 2.3. Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using an Agilent 400 MHz Varian spectrometer in CDCl<sub>3</sub>. <sup>1</sup>H NMR chemical shifts in CDCl<sub>3</sub> were referenced to CHCl<sub>3</sub> (7.27 ppm) and <sup>13</sup>C NMR chemical shifts in CDCl<sub>3</sub> were reported relative to CHCl<sub>3</sub> (77.23 ppm). UV-visible spectra were recorded on a Beckman DU650 spectrophotometer. Fluorescence spectra were recorded on a Jasco FP-6500 spectrophotometer. Fluorescent quantum yields in the solid films were recorded on an Otsuka electronics QE-2000 spectrophotometer. For time-resolved PL spectroscopy, a femtosecond pulsed Ti:sapphire laser and a nanosecond pulsed Nd:YAG laser were employed as excitation light sources for a prompt component and a delayed component, respectively, and a monochromator-attached photomultiplier tube was used as an optical detection system. Mass spectra were obtained using matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF MS) from Bruker. High-resolution masses were measured by either fast atom bombardment (FAB) or electron ionization (EI) using a JEOL HP 5890 series. Analytical thin-layer chromatography was performed using Kieselgel 60F-254 plates from Merck. Column chromatography was carried out on Merck silica gel 60 (70-230 mesh). All solvents and reagents were commercially available and used without further purification unless otherwise noted. Decomposition temperatures  $(T_d)$  and glass transition temperatures  $(T_g)$ were obtained using Q-5000-IR thermogravimetric analysis (TGA) and DSC-Q-1000 differential scanning calorimetry (DSC), respectively. The TGA and DSC analyses were performed at 10 °C min<sup>-1</sup> under a nitrogen atmosphere.  $T_g$  was determined from the third heating scan. The electrochemical properties of T1B and T2B were studied using cyclic voltammetry (CV) in CH<sub>2</sub>Cl<sub>2</sub> solutions (1.00 mM) with 0.1 M tetra-n-butylammoniumhexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte. A glassy carbon electrode was employed as the working electrode and referenced to a Ag reference electrode. All potential values were calibrated against the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

#### 2.4. Computational calculation

The optimized geometries and frontier molecular orbital energy levels for T1B and T2B were obtained using density functional theory (DFT) calculations with the Gaussian 09 program package. The geometries were optimized using the Becke 3-parameter Lee–Yang–Parr (B3LYP) functional with the 6-311G-level atomic basis set.

# 2.5. Deep-blue FLOLEDs fabrication and electro-optical characterization

*N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (NPB), 4,4',4''-tris(N-carbazolyl)triphenylamine (TCTA), and 1,3,5tris(N-phenylbenzimidazol-2-yl)benzene (TPBI) were purchased from commercial sources and used without purification. Fabrication of organic light-emitting diodes (OLEDs) was conducted through high-vacuum ( $2 \times 10^{-6}$  Torr) thermal evaporation of the organic materials onto indium tin oxide (ITO)-coated glass (sheet resistance:  $15 \Omega$ /square; Applied Film Corp.). Glass substrates with patterned ITO electrodes were washed with isopropyl alcohol and then cleaned through O<sub>2</sub> plasma treatment. OLED devices were fabricated with a configuration of ITO/NPB/TCTA/T1B or T2B/TPBI/LIF/Al. NPB and TCTA as hole transporting layers, TPBI as an electron transporting layer, LiF and Al electrodes were deposited on the substrate in the order of sequence. The emission properties were determined using a PR-650 SpectraScan SpectraColorimeter as a source meter. Current-voltage characteristics were measured using a programmable electrometer equipped with current and voltage sources (Keithley 2400).

#### 3. Results and discussion

#### 3.1. Computational calculation

To predict the optimized geometries and frontier molecular orbital energy levels for T1B and T2B, DFT calculations were carried out with the B3LYP/6-311G level using Gaussian '09. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) distributions of T1B and T2B are shown in Fig. 1. The HOMOs of T1B and T2B were localized on the triphenylamine (TPA) unit, whereas the LUMOs of T1B and T2B were dispersed over the benzimidazole (BI) unit. DFT analysis indicates that the HOMO and LUMO energy levels of T1B and T2B are similar (5.23 eV and 1.60 eV, respectively, for T1B; 5.21 eV and 1.58 eV, respectively, for T2B) [18].

DFT analysis of the molecular conformation revealed that the phenyl ring at the 1-position of BI was twisted with respect to the BI plane, with a dihedral angle of 27.9°, whereas the phenyl ring at the 2-position of BI was twisted with respect to the BI plane with a dihedral angle of 59.3°. Furthermore, the conjugation length of T2B was similar to that of T1B because the phenyl moiety at the 2-position of BI was almost perpendicular to the TPA moiety, thereby increasing the steric bulkiness in T2B as compared to T1B. In general, bulky, nonplanar structures suppress the molecular packing through increased steric hindrance between molecules, thus decreasing the charge carrier transport and the excimer formation. Therefore, T2B-based devices [18–22].

#### 3.2. Synthesis

The synthetic routes and molecular structures of T1B and T2B are illustrated in Fig. 2. T1B and T2B comprise two main components: TPA as the donor moiety and BI as the acceptor moiety; these two components were connected through a phenyl linkage by the Suzuki coupling reaction [23,24]. In T1B, the TPA unit was directly linked to the *para* position of the 2-phenyl moiety of 1,2-diphenylbenzimidazole. However, in T2B, the two TPA units were attached to the *para* positions of the two pendant phenyl moieties of 1,2-diphenylbenzimidazole, which would suppress exciton quenching by limited molecular packing owing to the more bulky three-dimensional structure. Synthetic yields of the Suzuki reactions leading to T1B and T2B were 76% and 74%, respectively, after purification

by column chromatography and vacuum sublimation. T1B and T2B were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and lowand high-resolution mass data.

#### 3.3. Thermal properties

The thermal properties of T1B and T2B were investigated with TGA and DSC (Fig. 3).  $T_d$ , defined as the temperature at which 5% mass loss occurs, was measured by TGA. The  $T_d$ values of T1B and T2B were 362 and 475 °C, respectively, whereas their  $T_g$  values were 97 and 137 °C, respectively.  $T_g$  of T2B was increased by 40 °C by the additional TPA unit. This indicates that a T2B emitter would be much better than a T1B emitter in terms of thermal stability [25].

#### 3.4. Photophysical properties

Fig. 4 depicts the normalized UV–vis absorbance (at 300 K) and photoluminescence (PL) spectra (at 300 K and 77 K) of T1B and T2B. The absorption bands around 300 nm for T1B and T2B originate from the TPA-centered  $n-\pi^*$  transition [18]. The absorption bands around 350 nm are attributed to the intramolecular charge-transfer transition from the electron-donating TPA moiety to the electron-accepting BI moiety [18,26,27]. The absorption edges of the UV–vis spectra were found to be 420 nm, which corresponds to the optical bandgap of 2.95 eV. From the optical bandgap and the HOMO energy level of 5.33 eV estimated from CV, the LUMO energy level was calculated to be 2.38 eV.

The PL  $\lambda_{max}$  peaks of T1B and T2B were observed around 440 nm without any vibration peaks. Although an extra TPA unit was introduced at the *para* position of the pendant 2-phenyl group in T2B, the emission spectra of T1B and T2B display the identical maxima in both the solution



Fig. 1. DFT calculations of T1B and T2B were performed at B3LYP/6-311G level: (a) chemical structures, (b) three-dimensional optimized geometries, and (c) HOMO and LUMO electron density map.



Fig. 3. TGA thermograms of T1B and T2B (inset: DSC analysis of T1B and T2B).

Temperature (°C)

and the solid states. These results demonstrate that the additional TPA moiety connected to the *para* position of the pendant 2-phenyl group does not contribute to the extension of the conjugation length [19]. The nonplanar structures of T1B and T2B facilitate their use as emitters in nondoped deep-blue FLOLEDs owing to the efficient

inhibition of  $\pi$ - $\pi$  stacking in the film state by vapor deposition.

On going from singlet (300 K) to triplet (77 K) states in PL spectra, a red shift of 80 for T1B and 79 nm for T2B is observed, indicating the energy gap between the lowest excited singlet state and the lowest excited triplet state



**Fig. 4.** UV-vis absorption and photoluminescence (PL) spectra of (a) T1B and (b) T2B. (Dashed lines perpendicular to the *x*-axis correspond to  $\lambda_{max}$  of PL spectra.)

 $(\Delta E_{\rm ST})$  of 0.44 and 0.43 eV, respectively. It has been known that a small  $\Delta E_{ST}$  in aromatic organic compounds would facilitate the reverse intersystem crossing (RISC) even without heavy metals [28–31]. These  $\Delta E_{ST}$  values predict that the surrounding thermal energies may enable RISC in T1B and T2B, which could contribute to the increased device efficiency over the intrinsic limitations of fluorescent device performances. We investigated the emission lifetimes of T1B and T2B by using transient PL decay measurements in order to evaluate the possibility of RISC in terms of delayed fluorescence (Fig. S1). PL decay lifetimes of T1B and T2B are 1.72 ns and 1.75 ns for prompt fluorescence, and 8.33 µs and 8.52 µs for delayed fluorescence, respectively. Therefore, it is clear from these data that the delayed fluorescence originates from the RISC process despite the relatively large  $\Delta E_{ST}$  values.

The photoluminescence quantum yields (PLQYs) of T1B and T2B in solution were measured to be 0.72 and 0.66, respectively, using 9,10-di(naphth-2-yl)anthracene (AD-N,PLQY = 0.57) as a reference at room temperature [32]. The PLQYs of T1B and T2B in the solid state are 0.50 and 0.60, respectively. T2B showed only a 9.1% reduction in the PLQYs upon going from the solution to solid states, comparing with a 30.6% reduction in the case of T1B. These results indicate that T2B suppresses exciton quenching by limited molecular packing owing to the increased steric bulkiness of T2B compared to T1B.

#### 3.5. Electroluminescence properties

Nondoped FLOLEDs were fabricated using T1B and T2B as emitters in the EML, with a device configuration of ITO/ NPB (40 nm)/TCTA (20 nm)/EML (T1B or T2B, 40 nm)/TPBI (20 nm)/LiF (1 nm)/Al (100 nm). Two different blue FLOL-EDs, one using T1B and the other using T2B as a deep-blue emitter, were fabricated and the performance of each device was evaluated (Table 1).

Fig. 5a shows current density-voltage characteristics of deep-blue fluorescent devices with T1B and T2B. The current density of the device with T1B was higher than that of the device with T2B, whereas the luminance values of the two devices with T1B and T2B emitters are similar at the same driving voltage as shown in Fig. 5b. The current density mainly depends on the differences in the energy levels of the organic thin layers in OLEDs [33–35]. Despite little difference in the energy levels of both deep-blue emitters, there is a discrepancy in the current densities at the same voltage. It is known that efficient packing of semiconductor molecules usually facilitates better current flow through the devices [18]. Thus, the alternation of the packing densities in the solid films derived from the structurally different T1B and T2B would result in different current densities; the current density of the device with the structurally less bulky T1B was higher than that of the device with the structurally more bulky T2B. These results are consistent with our simulation using DFT calculations. Unlike the current density characteristics of T1B- and T2B-based devices, similar luminance values of the two devices indicate that exciton formation and light emission are more efficient in T2B-based devices (Fig. 5b).

Quantum efficiency–luminance of two devices was plotted in Fig. 5c based on current density and luminance of devices. The T2B-based device shows a better maximum EQE of 4.67% compared with that of 3.05% of the T1B-based device at 100 cd/m<sup>2</sup>. In the case of T2B-based devices, EQE

# Table 1 Electroluminescence (EL) device performance of T1B and T2B.

At 100 cd/m <sup>2</sup>	Current density (mA/cm <sup>2</sup> )	Quantum efficiency (%)	CIE(x,y)	EL $\lambda_{max}$
T1B	5.12	3.05	0.15, 0.08	452
T2B	3.13	4.67	0.15, 0.08	452



**Fig. 5.** Device performance of deep-blue FLOLEDs with T1B and T2B. (a) current density–voltage characteristics (inset: energy level diagram of the FLOLEDs), (b) luminance–voltage characteristics, (c) quantum efficiency–luminance characteristics and (d) electroluminescence spectra. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

is about 1.4 times higher than the theoretical maximum EOE of about 3.3%, assuming that the EL quantum efficiency is the same as the PL quantum efficiency of 66%. Relatively high EQEs of the T1B- and T2B-based devices are attributed to thermally activated delayed fluorescence (TADF) by RISC that converts triplet excitons into singlet excited states [30,36]. It has been known that such an unusual increase in EQE originates from the triplet-triplet annihilation (TTA) and TADF [37,38]. For the TTA, the luminance is known to increase more than linearly with an increase in the current density [39]. However, in the case of the TADF, which occurs in a fluorescent molecule containing a sufficiently separated HOMO and LUMO [31], the luminance increases linearly or less than linearly with an increase in the current density [30]. In the current work, the luminance showed a linear increase at very low current density, and then appeared to be saturated at high current density as shown in Fig. S2. Consequently, enhanced efficiency by delayed fluorescence is not due to the TTA, but due to the TADF. In addition, as expected from the molecular packing density of DFT simulations and the solid PLQYs of T1B and T2B, the T2B-based device has relatively fewer sites for exciton recombination with respect to molecular concentrations, resulting in a smaller exciton density as compared to the T1B-based device. However, concentrated excitons caused by more efficient packing would be more easily quenched in T1B. Therefore, the device performance based on T2B is superior to that of T1B-based devices.

Fig. 5d shows normalized EL spectra of the deep-blue fluorescent devices. A blue emission with a peak wavelength at 452 nm, which originated from the singlet excitons of blue emitters without any other emission from the adjacent layers, was observed in all devices. The EL spectra are essentially stable against changes in the molecular structure.

#### 4. Summary

Two triphenylamine-attached benzimidazole derivatives (T1B and T2B) were designed and synthesized for use as deep-blue emitters in efficient nondoped FLOLEDs. The fluorescent devices fabricated using T2B exhibited a high EQE of 4.67%, which is 1.4 times higher than the theoretical maximum EQE of 3.3%, along with the CIE coordinates of (0.15,0.08). Considering the high color purity of the blue emission, T2B affords high EQE among the nondoped FLOLEDs. This study demonstrates a good example of the fact that the limited molecular packing density of the emitter suppresses the exciton quenching, thereby increasing the EQE in the nondoped FLOLEDs.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.orgel.2013.06.022.

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