

Novel Electron-transport Material Containing Boron Atom with a High Triplet Excited Energy Level

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Tris-[3-(3-pyridyl)mesityl]borane (3TPYMB) with high triplet excited energy level was synthesized and investigated as an electron-transport material for organic light-emitting devices (OLEDs). Larger current density and higher luminance were observed for the OLED using 3TPYMB, compared with the OLED with a conventional electron-transport material, tris(8-quinolinolato)aluminum (Alq₃).

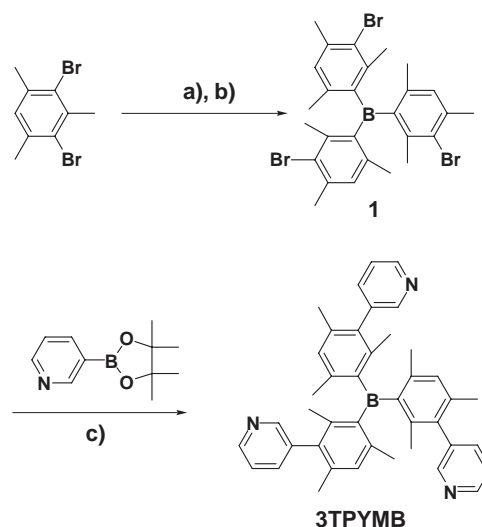
Three-coordinate boron atom, with its vacant p-orbital, is a strong π -electron acceptor in conjugated organic molecules. Therefore, organoboron compounds have been investigated as electron-transporting materials in organic light-emitting devices (OLEDs).^{1–3} Recently, OLEDs having phosphorescent emitters have received considerable attention, since such emitting materials can provide higher quantum efficiencies.^{4,5}

To achieve high efficiencies in OLEDs having phosphorescent emitters, it is important to suppress the transfer of the triplet excited energy from the phosphorescent emitter not only to the host material but also to the carrier transport materials adjacent to the emitting layer (EML). It is, therefore, necessary to use carrier transport materials with triplet energy levels higher than that of the phosphorescent emitter.

Concerning electron-transport materials (ETMs) for OLEDs, a variety of materials have been reported.^{6–8} However, there are few ETMs with sufficiently high triplet energy levels. From such a point of view, we synthesized a novel electron-transport material containing trimesitylborane unit, tris[3-(3-pyridyl)mesityl]borane (3TPYMB), with a wide HOMO–LUMO energy gap and a high triplet excited energy level. In designing the molecular structure, the following points were considered. First, because of boron atom with vacant p-orbital, we can expect a high electron affinity, resulting in reducing the barrier height for the electron injection from the cathode. Second, by introduction of electron-withdrawing units such as pyridine units, a high electron affinity is expected. Third, the twisted molecular structure, by the introduction of mesityl groups, leads to wide HOMO–LUMO energy gaps and high triplet excited energy levels.

Scheme 1 shows the chemical structure of 3TPYMB and the synthetic scheme. Compound **1** was prepared via monolithiation of 2,4-dibromomesitylene using 1.0 equiv. of *n*-butyllithium, followed by the reaction with boron trifluoride diethyl etherate in 70% yield. 3TPYMB was synthesized by palladium-catalyzed Suzuki coupling reaction of **1** with 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine.⁹ The crude material was purified by silica-gel column chromatography to give colorless glassy material (yield 87%). 3TPYMB was further purified by train sublimation method for the OLED application.

The glass transition temperature (*T*_g) of 3TPYMB was



a) *n*-BuLi 1 equiv., -78 °C → rt, 3 h

b) Boron trifluoride diethyletherate 1/3 equiv., -78 °C → rt, 12 h

c) Pd(PPh₃)₄, Toluene/EtOH, 2M Na₂CO₃ aq, 72 °C, 12 h

Scheme 1. Synthesis of 3TPYMB.

observed at 106 °C from differential scanning calorimetry analysis, which is high enough for OLED application. Crystallization of 3TPYMB was found to be suppressed in the solid state because of its twisted structure. Optoelectronic properties of Alq₃ and 3TPYMB are summarized in Table 1. Ionization potential (*I*_p) of 3TPYMB was determined to be 6.77 eV by photoelectron spectroscopy under ambient atmosphere, which is larger as compared to Alq₃, indicating high hole blocking ability of 3TPYMB. The HOMO–LUMO energy gap (*E*_g) of 3TPYMB was determined to be 3.45 eV from UV absorption edge, which can lead to high triplet energy level. Electron affinity (*E*_a) of 3TPYMB was estimated to be 3.32 eV, which is greater than that of Alq₃. Low barrier height for the electron injection from the cathode is expected.

Electron drift mobility of 3TPYMB and Alq₃ were determined by the time-of-flight method (Figure 1). The electron mobility of 3TPYMB was about 10^{–5} cm² V^{–1} s^{–1} order, which is

Table 1. Optoelectronic properties of 3TPYMB and Alq₃^a

	<i>I</i> _p /eV	<i>E</i> _g /eV	<i>E</i> _a /eV
3TPYMB	6.77	3.45	3.32
Alq ₃	5.93	2.71	3.22

^a*I*_p: measured by Riken Keiki AC-3, *E*_g: determined from UV absorption edge, *E*_a: calculated from *I*_p and *E*_g values.

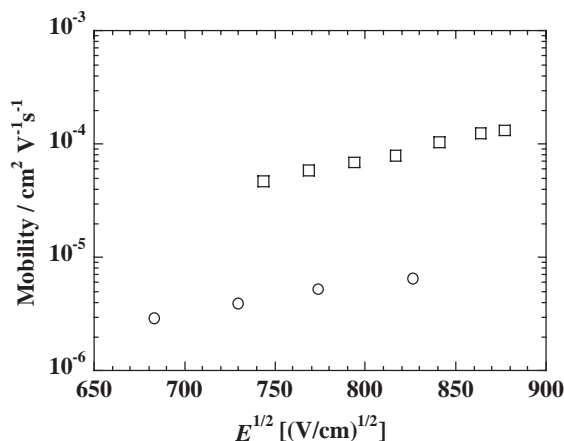


Figure 1. Electric field dependence of electron mobility for 3TPYMB (squares) and Alq₃ (circles).

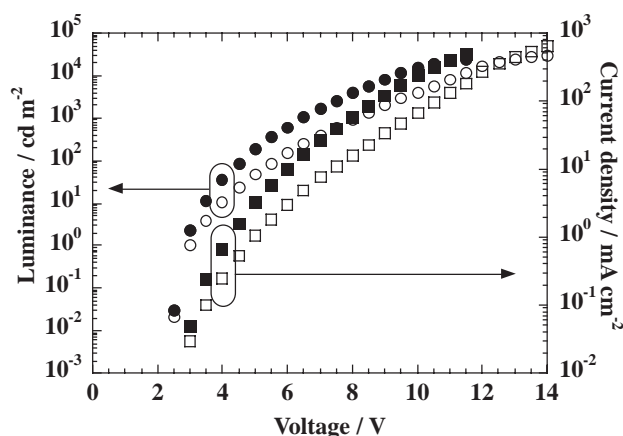


Figure 2. Luminance–voltage and current density–voltage characteristics for the NPD/Alq₃ (open) and NPD/Alq₃/3TPYMB (close) devices.

about 10 times higher than that of Alq₃. These results suggest that 3TPYMB can provide low drive voltages when used as the electron-transport layer in OLEDs.

3TPYMB was examined as an electron-transport layer of typical OLEDs consisting of [*N*-(1-naphthyl)-*N*-phenylamino]-biphenyl (NPD) and tris(8-hydroxyquinolinolato)aluminum (Alq₃) as a hole-transport layer and an electron-transporting emitter layer, respectively. OLEDs with a structure of ITO/NPD (50 nm)/Alq₃ (40 nm)/3TPYMB (30 nm)/LiF (0.5 nm)/Al (100 nm) (device I) was fabricated. As a reference, the device with a structure of ITO/NPD (50 nm)/Alq₃ (70 nm)/LiF (0.5 nm)/Al (100 nm) (device II) was also fabricated. All organic materials were vacuum deposited under 5.0×10^{-6} Torr. Lithium fluoride and aluminum were also deposited under 1.0×10^{-5} Torr.

Green emission from the Alq₃ layer was observed from the device I, using 3TPYMB as the electron-transport layer, which indicates that 3TPYMB has hole-blocking property. Figure 2 shows current density–voltage and luminance–voltage characteristics of both devices. The device I exhibits larger current

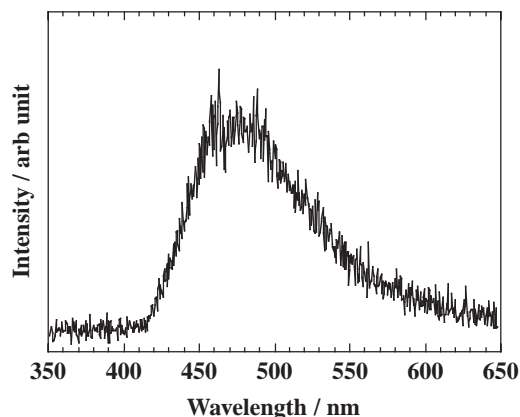


Figure 3. Phosphorescence spectrum of a vacuum deposited 3TPYMB film at 4.2 K, measured by streak camera with a N₂ gas laser (337 nm) as an excitation source.

densities and higher luminance at the same driving voltages compared with the device II. Such low drive voltages of the device I are due to the low LUMO level of 3TPYMB, resulting in the reduction of the barrier height for the electron injection from the cathode and to the high electron mobility of 3TPYMB.

Figure 3 shows phosphorescence spectrum of 3TPYMB. The onset of 3TPYMB phosphorescence was observed at about 420 nm, which is equivalent to the excited energy level of 2.95 eV. Therefore, it is considered that 3TPYMB is useful for OLEDs having phosphorescent emitter.

In conclusion, a novel trimesitylborane compound, 3TPYMB, was synthesized. 3TPYMB has high electron mobility of $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and high triplet excited energy level of 2.95 eV. It was also demonstrated to be useful as the electron-transport layer in OLEDs.

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References and Notes

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- 9 **3TPYMB**: ¹H NMR (270 MHz, CDCl₃) δ 1.70–1.85 (m, 9H), 1.93–2.14 (m, 18H), 6.89 (dd, 3H, $J = 5.94, 16.2 \text{ Hz}$), 7.31–7.50 (m, 6H), 8.29–8.39 (m, 3H), 8.54–8.58 (m, 3H); EI-MS: Calcd MW, 599.6; $m/z = 600 \text{ (M}^+)$, 585, 402, 387, 372, 300, 197, 182, 167. Anal. Calcd for C₄₂H₄₂BN₃: C, 84.13; H, 7.06; B, 1.80; N, 7.01%. Found: C, 83.84; H, 7.06; N, 6.93%.