

1,3-Bis[5-(dimesitylboryl)thiophen-2-yl]benzene and 1,3,5-Tris[5-(dimesitylboryl)thiophen-2-yl]benzene as a Novel Family of Electron-Transporting Hole Blockers for Organic Electroluminescent Devices

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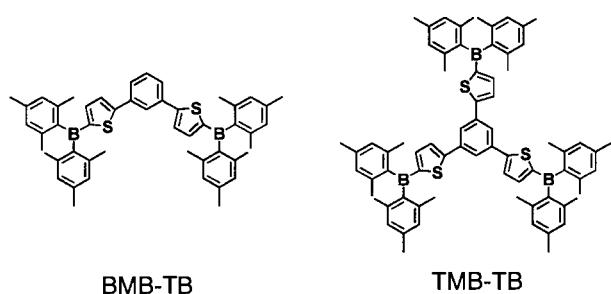
A novel family of electron-transporting hole blockers, 1,3-bis[5-(dimesitylboryl)thiophen-2-yl]benzene and 1,3,5-tris[5-(dimesitylboryl)thiophen-2-yl]benzene (TMB-TB), were designed and synthesized. They were found to exhibit multiple redox behavior in electrochemical reduction and to readily form stable amorphous glasses with high glass-transition temperatures above 100 °C. TMB-TB was proven to function well as a hole blocker in blue-emitting organic electroluminescent devices.

The performance of organic electroluminescent (EL) devices depends on materials functioning in various specialized roles, including charge-transporting materials which are required to facilitate charge injection from the electrodes into the emitting layer.

Amorphous molecular materials that form uniform amorphous thin films have been found to be well suited for use in organic EL devices.¹ As compared with hole-transporting materials, there are fewer known examples of electron-transporting materials. They include tris(8-quinolinolato)aluminum (Alq_3),²⁻⁴ oxadiazole and triazole derivatives,⁵⁻⁷ 1,1-dimethyl-2,5-di(2-pyridyl)silole,⁸ but their morphologies have not been reported in detail. Thermally and morphologically stable electron-transporting amorphous molecular materials, 5,5'-bis(dimesitylboryl)-2,2'-bithiophene and 5,5'-bis(dimesitylboryl)-2,2':5',2"-terthiophene, perform well as buffer layer materials for facilitating electron injection from the cathode into a layer of Alq_3 functioning as the emitter.⁹ However, in devices using in particular emitting layers with hole-transporting characteristics, an additional need for blocking holes from escaping from them arises. Bathocuproine has recently been reported to serve as a hole blocker, but its morphology and thermal stability are also unknown.⁴ It is a subject of current importance to develop new materials that both transport electrons and block holes.

We report here the creation of a new class of electron-transporting amorphous molecular materials that function as effective hole blockers, 1,3-bis[5-(dimesitylboryl)thiophen-2-yl]benzene (BMB-TB) and 1,3,5-tris[5-(dimesitylboryl)thiophen-2-yl]benzene (TMB-TB). These materials are characterized by the formation of stable amorphous glasses with high glass-transition temperatures (T_g s) above 100 °C, reversibility of cathodic reduction, multiple redox processes, almost the same reduction potentials as that of Alq_3 , and better hole-blocking character than Alq_3 .

The new compounds, BMB-TB and TMB-TB, were synthesized by the reaction of dimesitylboron fluoride with lithiated 1,3-di(2-thienyl)benzene or 1,3,5-tri(2-thienyl)benzene in THF at 0 °C under nitrogen atmosphere in ca. 15% and 12% yields, respectively.¹⁰



BMB-TB

TMB-TB

Both BMB-TB and TMB-TB, which were obtained as polycrystals by recrystallization from solution, were found to form stable amorphous glasses with T_g s of 109 and 160 °C, respectively, when the melt samples were cooled on standing in air, as evidenced by differential scanning calorimetry, X-ray diffraction, and polarized light microscopy. They also form uniform amorphous thin films by vacuum deposition.

These two compounds fulfill the requirement of reversible cathodic reduction for electron-transporting materials. In addition, it is of interest to note that both BMB-TB and TMB-TB have multiple redox properties, exhibiting two and three sequential cathodic and the corresponding anodic waves, respectively, in their cyclic voltammograms (Figure 1). The half-wave reduction potentials ($E_{1/2}^{\text{red}}$) of BMB-TB and TMB-TB were determined to be -2.03 and -1.98 V vs Ag/Ag^+ (0.01 mol dm⁻³), respectively. These reduction potentials are almost the same as that of Alq_3 ($E_{1/2}^{\text{red}} = -2.01$ V vs Ag/Ag^+ (0.01 mol dm⁻³)), and hence, BMB-TB and TMB-TB are expected to function as materials for facilitating electron injection from the cathode into the emitting layer in organic EL devices.

BMB-TB and TMB-TB show electronic absorption bands with a maximum at 371 (log $\epsilon = 4.8$) and 368 nm (log $\epsilon = 4.9$), respectively, in THF solution. The energy band gaps of both BMB-TB and TMB-TB are estimated from the energy thresholds of their electronic absorption spectra to be 3.2 eV, which is 0.5 eV wider than that of Alq_3 (2.7 eV). Since the LUMO levels of BMB-TB and TMB-TB are thought to be almost the same as that of Alq_3 (3.1 eV), the HOMO levels of BMB-TB and TMB-TB are estimated to lie at ca. 6.3 eV, which is 0.5 eV greater than that of Alq_3 (5.8 eV). Therefore, both BMB-TB and TMB-TB are expected to function as better hole blockers than Alq_3 .

In order to develop blue-emitting organic EL devices, triple-layer devices using 4,4',4"-tris(3-methylphenyl(phenyl)-amino)triphenylamine (*m*-MTDATA) as the hole transporter, tri(*p*-terphenyl-4-yl)amine (*p*-TTA) as the blue emitter, and Alq_3 or TMB-TB as the electron transporter were fabricated by sequential vacuum deposition of the organic materials onto an ITO-coat-

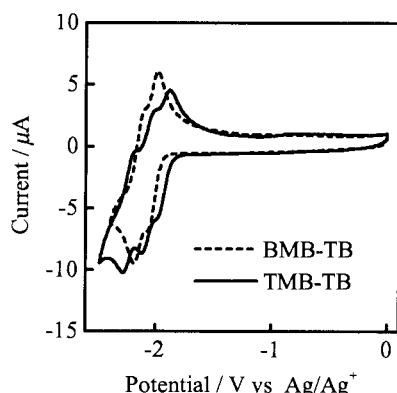


Figure 1. Cyclic voltammograms of BMB-TB (dashed line) and TMB-TB (solid line) in tetrahydrofuran (1.0×10^{-3} mol dm^{-3}) containing tetra-*n*-butylammonium perchlorate (0.1 mol dm^{-3}). Working, counter, and reference electrodes: platinum disk (1.6 mm in diameter), platinum wire, and Ag/AgNO_3 (0.01 mol dm^{-3} in acetonitrile). Scan rate: 500 mV s^{-1} .

ed glass substrate at a deposition rate of 1–2 \AA s^{-1} at 10^{–5} Torr, followed by vacuum deposition of an alloy of magnesium and silver (ca. 10:1 in volume ratio) onto the electron-transport layer.

The device using Alq_3 as the electron-transport layer, ITO/*m*-MTDATA(300 \AA)/*p*-TTA(400 \AA)/ Alq_3 (300 \AA)/MgAg, began to emit at a driving voltage of 4 V. However, the emitted light was green, originating from Alq_3 instead of the desired blue emission originating from *p*-TTA. At higher driving voltage, the green light from Alq_3 still prevailed, although blue light from *p*-TTA also contributed to the overall emission (Figure 2a). This result indicates that holes injected from the ITO electrode into the *p*-TTA (HOMO level: 5.6 eV)¹¹ layer via the *m*-MTDATA layer enter the Alq_3 layer due to the lack of efficient hole blocking by Alq_3 .

Contrastingly, the device using TMB-TB as the electron transporter, ITO/*m*-MTDATA(300 \AA)/*p*-TTA(400 \AA)/TMB-TB(300 \AA)/MgAg, emitted bright blue light resulting from *p*-TTA (Figure 2b). The EL spectrum was in good accordance with the photoluminescence (PL) spectrum of a *p*-TTA thin film. The device began to emit at a driving voltage of 4 V, giving a maximum luminance of 1875 cdm^{-2} at a driving voltage of 20 V and an external quantum efficiency of 0.7% at a luminance of 300 cdm^{-2} . This triple-layer device exhibited eight times higher quantum efficiency than that of the corresponding double-layer device without the TMB-TB layer. These results indicate that TMB-TB serves both as the electron transporter and the hole blocker in blue-emitting organic EL devices using *p*-TTA as the emitter.

The brightness of the blue emission is enhanced by the doping of perylene into the *p*-TTA layer of the above triple-layer device. A perylene-doped triple-layer device, ITO/*m*-MTDATA(300 \AA)/5 mol% perylene-doped *p*-TTA(400 \AA)/TMB-TB(300 \AA)/MgAg, emitted bright blue light resulting from perylene. The EL spectrum, which is red-shifted relative to that of the undoped triple-layer device, is in good agreement with the PL spectrum of a dilute solution of perylene (Figure 2c). This device exhibited a maximum luminance of 4130 cdm^{-2} at a driving voltage of 17 V, a luminous efficiency of 0.48 lmW^{-1} , and an external quantum efficiency of 0.8% at a luminance of 300 cdm^{-2} .

In summary, a novel class of amorphous molecular materials that function as effective electron-transporting hole blockers, BMB-TB and TMB-TB, were created. They readily form stable

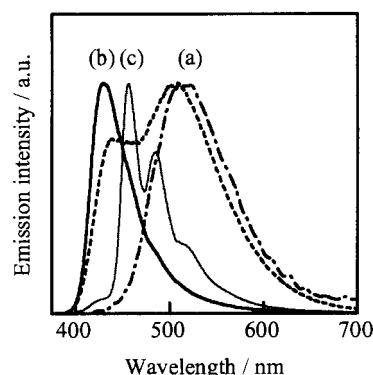


Figure 2. Electroluminescence spectra of triple-layer devices: (a) ITO/*m*-MTDATA(300 \AA)/*p*-TTA(400 \AA)/ Alq_3 (300 \AA)/MgAg (applied voltage: --- 4 V, ---- 6 V), (b) ITO/*m*-MTDATA(300 \AA)/*p*-TTA(400 \AA)/TMB-TB(300 \AA)/MgAg and (c) ITO/*m*-MTDATA(300 \AA)/5 mol% perylene-doped *p*-TTA(400 \AA)/TMB-TB(300 \AA)/MgAg.

amorphous glasses with high T_g s of 109°C and 160°C, respectively, and uniform amorphous thin films by vacuum deposition. TMB-TB was proven to function as an effective electron-transporting hole blocker for blue-emitting organic EL devices using *p*-TTA as an emitter. The brightness was improved by the doping of perylene. The present study paves the way for the development of further new amorphous molecular materials that function as electron-transporting hole blockers.

References and Notes

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- BMB-TB: mp 221 °C. MS(EI) : m/z = 738 (M^+). ^1H NMR (750 MHz, CDCl_3) (ppm) 2.14 (24H, s), 2.30 (12H, s), 6.83 (8H, s), 7.34 (1H, t, J = 7.8), 7.41 (2H, d, J = 3.7), 7.47 (2H, d, J = 3.8), 7.58 (2H, dd, J = 7.8), 7.91 (1H, s). Anal. Calcd for $\text{C}_{50}\text{H}_{52}\text{B}_2\text{S}_2$: C, 81.3; H, 7.10; B, 2.93; S, 8.68%. Found: C, 81.1; H, 7.26; S, 8.54%.
TMB-TB: mp 298 °C. MS(EI) : m/z = 1068 (M^+). ^1H NMR (600 MHz, $\text{THF}-d_8$) (ppm) 2.13 (36H, s), 2.28 (18H, s), 6.82 (12H, s), 7.41 (3H, d, J = 3.8), 7.77 (3H, d, J = 3.5), 8.00 (3H, s). Anal. Calcd for $\text{C}_{72}\text{H}_{75}\text{B}_3\text{S}_3$: C, 80.9; H, 7.07; B, 3.03; S, 9.00%. Found: C, 80.72; H, 7.22; S, 9.03%.
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