J. Am. Chem. Soc. **1998,** *120,* 9714−9715

5,5′-Bis(dimesitylboryl)-2,2′-bithiophene and 5,5″-Bis(dimesitylboryl)-2,2′:5′,2″-terthiophene as a Novel Family of Electron-Transporting Amorphous Molecular Materials

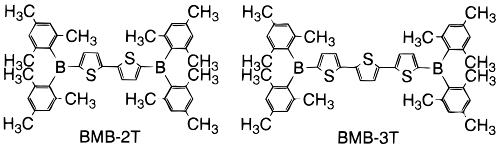
Tetsuya Noda and Yasuhiko Shirota*

Department of Applied Chemistry, Faculty of Engineering
Osaka University, Yamadaoka, Suita, Osaka 565-0871, Japan

Received May 18, 1998

Most of the amorphous molecular materials hitherto reported have electron-donating properties, functioning as hole-transporting materials in organic LEDs.[1−17] By contrast, there have been few reports on electron-accepting amorphous molecular materials that function as electron-transporting materials in organic LEDs. Oxadiazole derivatives,[16,18,19] 3-(biphenyl-4-yl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole,[20] and 1,1-dimethyl-2,5-di(2-pyridyl)-silole[21] have been reported to function as electron-transporting materials in organic LEDs although their glass-forming properties and morphological changes have not been reported in detail. For the fabrication of high-performance organic LEDs, hole- and electron-transporting materials as well as emitting materials are required. Developing electron-transporting amorphous molecular materials is a subject of current interest and significance.

We report here a novel family of thermally stable, electron-transporting amorphous molecular materials containing the bithiophene or terthiophene and dimesitylboryl moieties, 5,5′-bis(dimesitylboryl)-2,2′-bithiophene (BMB-2T) and 5,5″-bis(dimesitylboryl)-2,2′:5′,2″-terthiophene (BMB-3T). We have designed molecules containing an oligothiophene moiety including bithiophene and terthiophene, considering the following aspects. The presence of a π-electron system is essential for charge-carrier transport. Oligothiophenes may function as either hole-transporting or electron-transporting materials, depending on the nature of the substituents. The incorporation of the dimesitylboryl moiety is intended to provide electron-accepting properties (half-wave reduction potential of trimesitylboron: −1.94 V vs SCE)[22] and to prevent ready crystallization of oligothiophenes by its nonplanar molecular structure. These compounds are found to readily form stable amorphous glasses with high glass-transition temperatures (Tgs) of 107 and 115 °C, respectively, and to function as excellent electron-transporting materials in organic LEDs. These novel electron-transporting amorphous molecular materials are totally different in molecular architecture from the hitherto reported electron-transporting materials based on heteroaromatic rings such as oxadiazole and triazole.



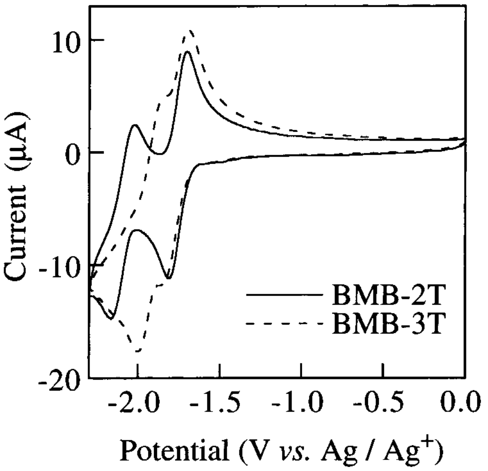


Figure 1. Cyclic voltammograms of BMB-2T (solid line) and BMB-3T (dashed line) (1.0×10^{-3} mol dm^{-3}) in tetrahydrofuran containing tetra-*n*-butylammonium perchlorate (0.1 mol dm^{-3}). Cyclic voltammetry was carried out using a platinum disk (1.6 mm in diameter) and a platinum wire as the working and counter electrodes, respectively, and Ag/AgNO$_3$ (0.01 mol dm^{-3} in acetonitrile) as the reference electrode. Scan rate: 500 mV s^{-1}.

The new compounds, BMB-2T and BMB-3T, were synthesized by the reaction of dimesitylboron fluoride with lithiated oligothiophenes in tetrahydrofuran under a nitrogen atmosphere in 40 and 30% yields, respectively, according to similar reactions using dimesitylboron fluoride.[23] They were purified by silica gel column chromatography, followed by recrystallization from benzene/*n*-hexane (volume ratio: 1:1) to give light yellow crystals and orange plate crystals for BMB-2T and BMB-3T. They were identified by various spectroscopies, mass spectrometry, and elemental analysis.[24]

Both BMB-2T and BMB-3T undergo reversible cathodic reductions. Figure 1 shows the cyclic voltammograms for the cathodic reductions of BMB-2T and BMB-3T. Both compounds exhibited two sequential cathodic and the corresponding anodic

---

* To whom correspondence should be addressed. E-mail: shirota@ap.chem.eng.osaka-u.ac.jp.

(1) Shirota, Y.; Kobata, T.; Noma, N. *Chem. Lett.* **1989**, 1145.

(2) Higuchi, A.; Inada, H.; Kobata, T.; Shirota, Y. *Adv. Mater.* **1991**, *3*, 549.

(3) Ishikawa, W.; Inada, H.; Nakano, H.; Shirota, Y. *Chem. Lett.* **1991**, 1731.

(4) Higuchi, A.; Ohnishi, K.; Nomura, S.; Inada, H.; Shirota, Y. *J. Mater. Chem.* **1992**, *2*, 1109.

(5) Inada, H.; Shirota, Y. *J. Mater. Chem.* **1993**, *3*, 319.

(6) Naito, K.; Miura, A. *J. Phys. Chem.* **1993**, *97*, 6240.

(7) Kuwabara, Y.; Ogawa, H.; Inada, H.; Noma, N.; Shirota, Y. *Adv. Mater.* **1994**, *6*, 677.

(8) Kageyama, H.; Itano, K.; Ishikawa, W.; Shirota, Y. *J. Mater. Chem.* **1996**, *6*, 675.

(9) Noda, T.; Imae, I.; Noma, N.; Shirota, Y. *Adv. Mater.* **1997**, *9*, 239.

(10) Salbeck, J.; Yu, N.; Bauer, J.; Weissörtel, F.; Bestgen, H. *Synth. Met.* **1997**, *91*, 209.

(11) Thelakkat, M.; Schmidt, H.-W. *Adv. Mater.* **1998**, *10*, 219.

(12) Katsuma, K.; Shirota, Y. *Adv. Mater.* **1998**, *10*, 223.

(13) Stolka, M.; Yanus, J. F.; Pai, D. M. *J. Phys. Chem.* **1984**, *88*, 4707.

(14) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.

(15) Shirota, Y.; Kuwabara, Y.; Inada, H.; Wakimoto, T.; Nakada, H.; Yonemoto, Y.; Kawami, S.; Imai, K. *Appl. Phys. Lett.* **1994**, *65*, 807.

(16) Shirota, Y.; Kuwabara, Y.; Okuda, D.; Okuda, R.; Ogawa, H.; Inada, H.; Wakimoto, T.; Nakada, H.; Yonemoto, Y.; Kawami, S.; Imai, K. *J. Lumin.* **1997**, *72*−*74*, 985.

(17) Shi, J.; Tang, C. W. *Appl. Phys. Lett.* **1997**, *70*, 1665.

(18) Hamada, Y.; Adachi, C.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1992**, *31*, 1812.

(19) Bettenhausen, J.; Strohriegl, P. *Adv. Mater.* **1996**, *8*, 507.

(20) Kido, J.; Ohtaki, C.; Hongawa, K.; Okuyama, K.; Nagai, K. *Jpn. J. Appl. Phys.* **1993**, *32*, L917.

(21) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974.

(22) Schulz, A.; Kaim, W. *Chem. Ber.* **1989**, *122*, 1863.

(23) Branger, C,; Lequan, M.; Lequan, R. M.; Barzoukas, M.; Fort, A. *J. Mater. Chem.* **1996**, *6*, 555.

(24) BMB-2T: mp 261°C. MS *m*/*e* 662 (M$^+$). ^{1}H NMR (600 MHz, chloroform-d_1) δ (ppm) 7.38 (2H, d, $J = 3.7$), 7.34 (2H, d, $J = 3.7$), 6.82 (8H, s), 2.30 (12H, s), 2.13 (24H, s). Anal. Calcd for $C_{44}H_{48}B_2S_2$ C, 79.76; H, 7.30; B, 3.26; S, 9.68. Found C, 79.62; H, 7.38; S, 9.68. UV: λ_{max} at 402 nm (log ϵ = 4.73). BMB-3T: mp 271 °C. MS *m*/*e* 744 (M$^+$). ^{1}H NMR (750 MHz, dioxane-d_8) δ (ppm) 7.41 (2H, d, $J = 3.7$), 7.37 (2H, d, $J = 3.7$), 7.35 (2H, s), 6.84 (8H, s), 2.28 (12H, s), 2.13 (24H, s). Anal. Calcd for $C_{48}H_{50}B_3S_2$ C, 77.41; H, 6.77; B, 2.90; S, 12.92. Found C, 77.19; H, 6.80; S, 12.81. UV: λ_{max} at 437 nm (log ϵ = 4.78).

S0002-7863(98)01734-X CCC: $15.00 © 1998 American Chemical Society
Published on Web 09/05/1998

Table 1. Performances of the Organic LEDs, ITO/*m*-MTDATA(300 Å)/α-NPD(200 Å)/Alq_3(500 Å)/MgAg and ITO/*m*-MTDATA(300 Å)/α-NPD(200 Å)/Alq_3(300 Å)/BMB-*n*T (*n* = 2 and 3)(200 Å)/MgAg[a]

device	maximum luminance (cd m^{-2})	luminous efficiency[d] (lm W^{-1})	quantum efficiency[d] (%)	current density[d] (mA cm^{-2})
m-MTDATA/α-NPD/Alq_3	13000[b]	1.4	0.9	13.7
m-MTDATA/α-NPD/Alq_3/BMB-2T	21400[c]	1.7	1.1	11.2
m-MTDATA/α-NPD/Alq_3/BMB-3T	23200[c]	1.5	1.1	12.6

[a] Current-voltage-luminance characteristics were measured with an electrometer (Advantest TR6143) and a luminance meter (Minolta LS-100). [b] At 16V. [c] At 17V. [d] For obtaining a luminance of 300 cd m^{-2}.

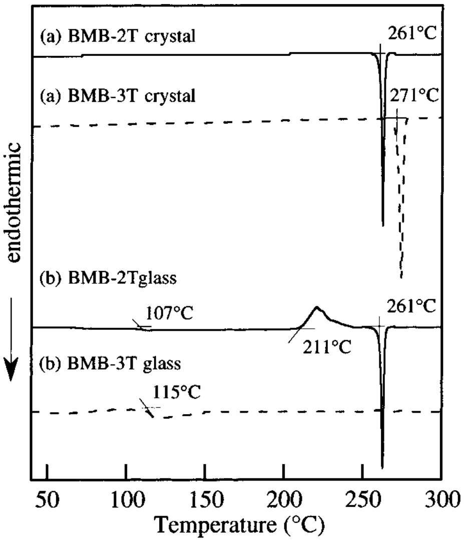


Figure 2. DSC curves of BMB-2T (solid line) and BMB-3T (dashed line). (a) Crystalline sample obtained by recrystallization from benzene/*n*-hexane, (b) glass sample obtained by cooling the melt. Heating rate: 5 °C min^{-1}.

waves, generating the radical anion and dianion species. The first half-wave reduction potentials ($E_{1/2}^{red}$) of BMB-2T and BMB-3T were almost the same irrespective of the difference in the conjugation length of the oligothiophene moiety, being −1.76 V vs Ag/Ag^+ (0.01 mol dm^{-3}). BMB-2T and BMB-3T have stronger electron-accepting properties than the oxadiazole derivatives (1,3,5-tris(4-*tert*-butylphenyl-1,3,4-oxadiazolyl)benzene: $E_{p/2}^{red}$ = −2.07 V vs Ag/Ag^+ (0.01 mol dm^{-3})).

In contrast to the crystalline nature of oligothiophenes due to their planar molecular structures,[25] BMB-2T and BMB-3T were found to readily form stable amorphous glasses when the melt samples were cooled on standing in air. It is thought that glass formation is due to the incorporation of the nonplanar dimesitylboryl group. The formation of the glassy state was evidenced by differential scanning calorimetry (DSC), X-ray diffraction, and polarizing microscopy. Figure 2 shows the DSC curves of BMB-2T and BMB-3T. When the crystalline sample of BMB-2T was heated, an endothermic peak due to melting was observed at 261 °C. When the melt sample was cooled, it formed a transparent, stable amorphous glass via a supercooled liquid state. When the glass sample was again heated, glass transition took place at 107 °C. On further heating above the Tg, crystallization took place at around 211 °C to give the same crystal as obtained by recrystallization from benzene/*n*-hexane, which melted at 261 °C. In the case of the BMB-3T glass, no crystallization behavior was observed on further heating above the Tg (115 °C) even at a very slow heating rate of 1 °C min^{-1}. Both the BMB-2T and BMB-3T glasses are stable in an ambient atmosphere containing oxygen and moisture.

Both BMB-2T and BMB-3T, which form uniform amorphous films by vacuum deposition, were found to function as excellent electron-transporting materials in organic LEDs. Organic LEDs using BMB-2T or BMB-3T as an electron-transporting material, tris(8-quinolinolato)aluminum (Alq_3)[14] as an emitting material, and 4,4′,4″-tris(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA)[1,15,16] and *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenyl-[1,1′-biphenyl]-4,4′-diamine (α-NPD)[17] as hole-transporting materials were fabricated by vacuum deposition and their performances examined in comparison with the device in the absence of the BMB-*n*T (*n* = 2 and 3) layer.

The organic LEDs, ITO/*m*-MTDATA(300 Å)/α-NPD(200 Å)/Alq_3(300 Å)/BMB-*n*T (*n* = 2 and 3)(200 Å)/MgAg, exhibited rectification behavior and emitted bright green light when a positive voltage was applied to the ITO electrode. The electroluminescence spectra for the LEDs were in accord with the photoluminescence (fluorescence) spectrum of Alq_3. This result indicates that the electroluminescence originates from the singlet excited state of Alq_3 generated by the recombination of holes and electrons and that the BMB-*n*T (*n* = 2 and 3) function as the electron-transport layer. That is, the electron injection from the MgAg electrode into Alq_3 and the hole-injection from the ITO electrode into Alq_3 take place by the stepwise process via the BMB-*n*T layer and via the *m*-MTDATA and α-NPD layers, respectively. No crystallization phenomena of the materials were observed during use in LEDs.

As Table 1 shows, the LEDs using BMB-*n*T (*n* = 2 and 3) as the electron-transport layer exhibited definitely higher performances, approximately 10 to 20% higher luminous and quantum efficiencies, and 1.6 to 1.8 times higher maximum luminance than the LED without the BMB-*n*T layer, ITO/*m*-MTDATA(300 Å)/α-NPD(200 Å)/Alq_3(500 Å)/MgAg. The results show that the BMB-*n*T (*n* = 2 and 3) function as excellent electron-transporting materials in organic LEDs.

In summary, a novel family of electron-transporting amorphous molecular materials with high Tgs, BMB-2T and BMB-3T, have been created. They function as excellent electron-transporting materials in organic LEDs. The present study presents a new guideline for the molecular design of electron-transporting amorphous molecular materials, paving the way for the development of further new electron-transporting amorphous molecular materials.

JA9817343

---

(25) Servet, B.; Ries, S.; Trotel, M.; Alnot, P.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1993**, *5*, 461.