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A Novel Class of Emitting Amorphous Molecular Materials as Bipolar Radical Formants: 2-{4-[Bis(4-methylphenyl)amino]phenyl}-5-(dimesitylboryl)thiophene and 2-{4-[Bis(9,9-dimethylfluorenyl)amino]phenyl}-5-(dimesitylboryl)thiophene

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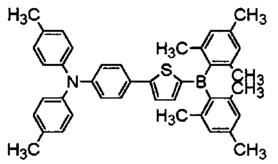
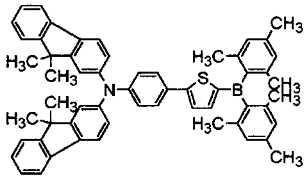
Amorphous molecular materials have demonstrated their suitability and versatility for use in organic light-emitting diodes (OLEDs).[1] In this work, we focused our attention to the design and synthesis of a new and better generation of emitting materials. In any type of OLEDs consisting of a single emitting layer or of multilayers using additional charge-transport layers, the emitting layer functions as the recombination center for the holes and electrons injected from the anode and cathode. The generated electronically excited-state molecule of the emitting layer either emits luminescence or serves as a host that transfers its excitation energy to a luminescent dopant. Therefore, materials for use in the emitting layer should meet the requirements of energy level matching for charge carrier injection and acceptance of both holes and electrons, and hence should desirably possess bipolar character to permit the formation of both stable cation and anion radicals. In addition, the emitting materials should form homogeneous thin films and exhibit intense fluorescence. The fulfillment of these material requirements is expected to lead to enhanced performance and operational stability of OLEDs.

Tris(8-quinolinolato)aluminum (Alq_3) has been most widely used as a green emitter or a host material for luminescent dopants.[2] It undergoes reversible reduction, but its anodic oxidation is irreversible.[3] The instability of the Alq_3 cation radical leads to the long-term degradation of Alq_3-based OLEDs, causing a significant decrease in the luminescence efficiency.[4] Other emitting materials, including only scarce examples of materials with bipolar character, e.g., compounds having an 1,3,4-oxadiazole moiety, have also been reported.[5−10] However, redox properties of most of the reported materials for the emitting layer have not been studied in any detail, some materials undergoing irreversible oxidation or reduction. Ruthenium(II) complexes have bipolar character,[9] but do not form uniform thin films by themselves.



PhAMB-1T

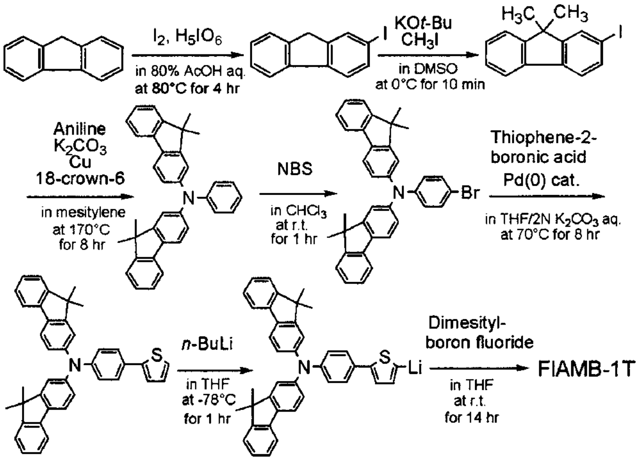


FlAMB-1T

We present here synthesis and characterization of a novel class of high-performance blue-green and green emitting amorphous molecular materials, 2-{4-[bis(4-methylphenyl)amino]phenyl}-5-(dimesitylboryl)thiophene (PhAMB-1T) and 2-{4-[bis(9,9-dimethylfluorenyl)amino]phenyl}-5-(dimesitylboryl)thiophene (FlAMB-1T). To the best of our knowledge, these materials are the first definite examples having the desired bipolar radical formant character that allows both stable cation and anion radicals, intense fluorescent characteristics, and the capability to form stable amorphous glasses with high glass-transition temperatures (T_gs) and uniform thin films by vacuum deposition.

These novel emitting amorphous molecular materials are different in molecular architecture from the hitherto reported emitting materials containing heteroaromatic rings such as oxadiazole[6] or triazole.[7] The incorporation of the triphenylamine and dimesitylboryl moieties, which are π-conjugated through the thiophene ring, is intended to provide both electron-donating and -accepting properties, respectively, and to facilitate formation of amorphous glasses due to their nonplanar molecular structures.

Scheme 1



PhAMB-1T and FlAMB-1T were synthesized by the reaction of dimesitylboron fluoride with lithiated *N*,*N*-bis(4-methylphenyl)-4-(2-thienyl)aniline or *N*,*N*-bis(9,9-dimethylfluorenyl)-4-(2-thienyl)-aniline in tetrahydrofuran (THF) under nitrogen atmosphere in ca. 50% yield. The synthetic procedure of FlAMB-1T is shown in Scheme 1. These compounds were purified by silica gel column chromatography, followed by recrystallization from solution, and identified by various spectroscopic methods, mass spectrometry, and elemental analysis.[11,12]

PhAMB-1T and FlAMB-1T display intense blue-green and green fluorescence, respectively. The electronic absorption and fluorescence spectra of PhAMB-1T and FlAMB-1T in a THF

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(1) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1 and references therein.

(2) (a) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610.

(3) Papadimitrakopoulos, F.; Zhang, X.-M.; Thomsen III, D. L.; Higginson, K. A. *Chem. Mater.* **1996**, *8*, 1363.

(4) Popovic, Z. D.; Aziz, H.; Hu, N.-X.; Hor, A.-M.; Xu, G. *Synth. Met.* **2000**, 111−112, 229.

(5) (a) Hamada, Y.; Sano, T.; Fujita, M.; Fujii, T.; Nishio, Y.; Shibata, K. *Jpn. J. Appl. Phys.* **1993**, *32*, L514. (b) Hamada, Y.; Sano, T.; Fujii, H.; Nishio, Y.; Takahashi, H.; Shibata, K. *Jpn. J. Appl. Phys.* **1996**, *35*, L1339.

(6) (a) Hamada, Y.; Adachi, C.; Tetsuo, T.; Saito, S. *Jpn. J., Appl. Phys.* **1992**, *31*, 1812. (b) Tamoto, N.; Adachi, C.; Nagai, K. *Chem. Mater.* **1997**, *9*, 1077. (d) Antoniadis, H.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 3055.

(7) Kido, J.; Kimura, M.; Nagai, K. *Chem. Lett.*, **1996**, 47.

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

(9) (a) Lyons, C. H.; Abbas, E. D.; Lee, J.-K.; Rubner, M. F. *J. Am. Chem. Soc.*, **1998**, *120*, 12100. (b) Gong, X.; Ng, P. K.; Chan, W. K. *Adv. Mater.* **1998**, *10*, 1337. (c) Handy, E. S.; Pal, A. J.; Rubner, M. F. *J. Am. Chem. Soc.*, **1999**, *121*, 3525.

(10) (a) Noda, T.; Ogawa, H.; Noma, N.; Shirota, Y. *Adv. Mater.* **1997**, *9*, 720. (b) Noda, T.; Ogawa, H.; Shirota, Y. *Adv. Mater.* **1999**, *11*, 283.

(11) PhAMB-1T: MS: *m*/*e* 603 (M^+). ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.48 (2H, d, $J = 8.5$), 7.38 (1H, d, $J = 3.7$), 7.34 (1H, d, $J = 3.7$), 7.07 (4H, d, $J = 8.3$), 7.00 (4H, d, $J = 8.3$), 6.96 (2H, d, $J = 8.5$), 6.82 (4H, s), 2.31 (6H, s), 2.30 (6H, s), 2.17 (12H, s). Anal. Calcd for $C_{42}H_{42}BNS$: C, 83.57; H, 7.01; N, 2.32, B, 1.79; S, 5.31. Found: C, 83.44; H, 7.14; N, 2.36; S, 5.30.

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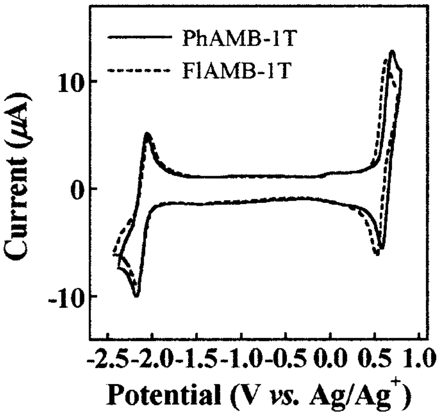

Figure 1. Cyclic voltammograms of PhAMB-1T (solid line) and FlAMB-1T (dashed line) (1.0×10^{-3} mol dm^{-3}) in tetrahydrofuran containing tetra-*n*-butylammonium perchlorate (0.1 mol dm^{-3}). Cyclic voltammetry was carried out using a platinum disk (1.6 mm in diameter) and a platinum wire as the working 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}.

solution show bands with maxima (λ_{max}) at 423 (log $\epsilon = 4.6$) and 515 nm (fluorescence quantum yield $\phi_f = 0.58$) and with λ_{max} at 435 (log $\epsilon = 4.6$) and 537 nm ($\phi_f = 0.50$), respectively. These bands are understood in terms of intramolecular charge transfer from the electron-donating triphenylamine or bifluorenylamine moiety to the electron-accepting dimesitylboryl moiety.

PhAMB-1T and FlAMB-1T possess the desired bipolar character, generating stable cation and anion radicals. Figure 1 shows cyclic voltammograms of PhAMB-1T and FlAMB-1T. Both compounds showed reversible redox properties, exhibiting one anodic and cathodic wave on oxidation and reduction, respectively, together with the corresponding cathodic and anodic waves. The half-wave oxidation and reduction potentials were 0.62 and -2.13 V vs Ag/Ag$^+$ (0.01 mol dm^{-3}) for PhAMB-1T and 0.58 and -2.01 V vs Ag/Ag$^+$ (0.01 mol dm^{-3}) for FlAMB-1T. When the scan was repeated in the region between -2.4 and 0.8 V vs Ag/Ag$^+$ (0.01 mol dm^{-3}), the same trace was obtained.

The new materials readily form stable amorphous glasses. While FlAMB-1T was obtained as polycrystals by recrystallization from THF/ethanol, PhAMB-1T was obtained as amorphous powders despite attempted recrystallization from solution. Differential scanning calorimetry performed on a crystalline sample of FlAMB-1T showed that upon heating, it melted at 274 °C to give an isotropic liquid. When the isotropic liquid was cooled on standing in air, it formed a transparent, stable amorphous glass via a supercooled liquid state. When the glass sample was again heated, glass transition took place at 124 °C. Likewise, the PhAMB-1T glass exhibited a T_g of 84 °C. The formation of the glassy state was also evidenced by X-ray diffraction and polarizing microscopy. While the crystalline sample of FlAMB-1T showed sharp peaks characteristic of the crystal, the amorphous glasses of PhAMB-1T and FlAMB-1T showed only a broad halo in their X-ray diffraction patterns. The glassy state of these materials is very stable, no crystallization being observed even on heating above their T_gs.

Triple-layer OLEDs using 4,4′,4″-tris[3-methylphenyl(phenyl)-amino]triphenylamine (*m*-MTDATA)[13] as a hole-transport layer, PhAMB-1T or FlAMB-1T as an emitting layer, and Alq$_3$ or 5,5′-bis(dimesitylboryl)-2,2′-bithiophene (BMB-2T)[14] as an electron-transport layer were fabricated by sequential vacuum deposition of organic materials onto an indium−tin-oxide (ITO)-coated glass substrate at a deposition rate of 2−3 Å s^{-1} at 10^{-5} Torr, followed by vacuum deposition of an alloy of magnesium and silver (volume ratio: ca. 10:1) onto the electron-transport layer. The fabricated devices, ITO/*m*-MTDATA(300 Å)/PhAMB-1T(200 Å)/Alq$_3$(300 Å)/MgAg (device a) and ITO/*m*-MTDATA(300 Å)/FlAMB-1T(200 Å)/BMB-2T(300 Å)/MgAg (device b), emitted bright blue-green and green light, respectively, when a positive voltage was applied to the ITO electrode. The electroluminescence spectra of the two devices were in good agreement with the photoluminescence spectra of the films of PhAMB-1T and FlAMB-1T, respectively. These results indicate that the electroluminescence originates from the excited singlet state of PhAMB-1T for device a and FlAMB-1T for device b, generated by the recombination of holes and electrons injected from the ITO and MgAg electrodes into PhAMB-1T or FlAMB-1T by a stepwise process via the hole- and electron-transport layers, respectively.

The emission started at a driving voltage of 3 V for both devices. The devices exhibited high performance with a maximum luminance of 12500 cd m^{-2} at a driving voltage of 16 V, a luminous efficiency of 1.1 lm W^{-1}, and an external quantum efficiency of 0.8% at a luminance of 300 cd m^{-2} for device a and a maximum luminance of 23700 cd m^{-2} at a driving voltage of 16 V, a luminous efficiency of 1.3 lm W^{-1}, and an external quantum efficiency of 1.0% at a luminance of 300 cd m^{-2} for device b. The maximum luminance of device b in particular is among the highest values compared with those reported for OLEDs in the absence of luminescent dopants.

The present study shows that the synthesized new materials, PhAMB-1T and FlAMB-1T, function as excellent blue-green and green emitting materials for OLEDs. They are also expected to serve as host materials for luminescent dopants. In addition, these bipolar emitting materials are expected to find a variety of applications, e.g. materials for organic light-emitting electrochemical cells and nonlinear optics.

In summary, a novel class of high-performance blue-green and green emitting amorphous molecular materials with the desired bipolar radical formant character, PhAMB-1T and FlAMB-1T, have been created. They have proven to function as excellent emitting materials for OLEDs. The present study presents a new guideline for the molecular design of emitting amorphous molecular materials, paving the way for the development of further new emitting amorphous molecular materials for various kinds of application.

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[12] FlAMB-1T: MS: m/e 807 (M$^+$). ^{1}H NMR (600 MHz, THF-d_8) δ (ppm): 7.69−7.61 (6H, m), 7.53 (1H, d, $J = 4.0$), 7.40 (2H, d, $J = 7.3$), 7.37 (2H, d, $J = 3.7$), 7.30 (2H, d, $J = 2.1$), 7.26 (2H, t, $J = 7.3$), 7.21 (2H, t, $J = 7.3$), 7.15 (2H, d, $J = 8.6$), 7.08 (2H, d, $J = 8.2$), 6.82 (4H, s), 2.27 (6H, s), 2.15 (12H, s), 1.40 (12H, s). Anal. Calcd for $C_{58}H_{54}BNS$: C, 86.22; H, 6.74; N, 1.73; B, 1.34; S, 3.97. Found: C, 86.27; H, 6.99; N, 1.73; S, 3.85.

[13] (a) Shirota, Y.; Kobata, T.; Noma, N. *Chem. Lett.* **1989**, 1145. (b) Shirota, Y.; Kuwabara, Y.; Inada, H.; Wakimoto, T.; Nakada, H.; Yonemoto, Y.; Kawami, S.; Imai, K. *Appl. Phys. Lett.* **1994**, *65*, 807.

[14] Noda, T.; Shirota, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9714.